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A CORRELATION OF PROPERTIES FOR VARIOUS FORMULATIONS OF SINTERED ZIRCONIA - UNPUBLISHED DATA

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 Since this is a progress report, the information herein is tentative and subjected to changes, corrections, and modifications.

ABSTRACT

This is the fourth quarterly report in a program designed to collect and disseminate previously unpublished materials data obtained during recent years by Chance Vought. The information contained in this report consists of mechanical and physical properties of various binary and ternary formulations of zirconia, a correlation of measured thermal shock data of zirconia with known thermal shock expressions, and interpretations of various criteria that are developed.

This is Volume III of a three volume report. The remaining volumes are as follows:

Volume I - CVC Report No. 2-53420/2R373	"Mechanical Properties of Some Engineering Materials - Unpublished Data from Company Sponsored Programs"
Volume II - CVC Report No. 2-53420/2R374	"Physical Properties of Some Engineering Materials - Unpublished Data from Company Sponsored Programs"

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INTRODUCTION

Zirconia has been selected for many rocket and missile applications due to its high refractoriness, high melting point, chemical stability, resistance to chemical attack including oxidation, and resistance to erosion imparted by its hardness. The data presented in this report were obtained in the development of a zirconia formulation for one of these missile applications.

The conditions imposed on the zirconia were quite severe. The zirconia must withstand temperatures in excess of 4300°F, repeated cycles to this temperature, appreciable time at this temperature, high loads, and erosive environments.

Thermal shock, expansion, emittance, strength, thermal conductivity and heat capacity data were required. A search of the literature provided only incomplete data at lower temperatures. Testing described in this report was therefore undertaken.

Since the development of a workable formulation was directed toward a specific use, the testing involved, especially on thermal shock, was usually confined to specific needs, as opposed to a research type operation where testing would be conducted over all ranges. Thermal shock resistance was measured for several grades of zirconia only at certain temperature levels. Additional approximations of thermal shock behavior of other formulations and at different temperatures were derived for this report from equations contained in the literature, utilizing estimated material properties such as strength, conductivity, Young's modulus, and the coefficient of thermal expansion. Correlations of experimentally observed versus estimated thermal shock behavior are presented.

This report contains a description of materials provided by the supplier, Zirconium Corporation of America, data obtained for Vought by Southern Research Institute, and data generated by Chance Vought. The cooperation of all parties is acknowledged, with particular credit to Messrs. R. L. Cox, I. E. Harder, H. H. Houston, J. T. Lynch, J. W. Seeger, and R. W. White.

FABRICATION OF MATERIALS

Zirconia in the pure state has a monoclinic crystal form. This form is stable up to approximately 1000°C, above which it inverts to the tetragonal form with considerable volume contraction. The reversal destructive volume change (expansion) occurs upon cooling. The addition of calcia, yttria, or other similar oxides (those that crystallize in the cubic form) to zirconia before firing may give cubic solid solutions that are partially or fully stabilized at essentially all temperatures. These stabilized zirconia materials were used for all the tests discussed in this report.

Zirconia materials used for all tests were fabricated into right circular solid cylinders, either by pressure molding around 5000 pounds per square inch, or extruding at less than 1000 pounds per square inch.

Formulations were made from zirconia with varying amounts of CaO, and from yttria and ceria at Zirconium Corporation of America, Solon, Ohio. Components of each formulation were added as fines or mixtures of fines and grog. The grog was prepared by fusing or firing (to 3250°F) the fines and then regrinding them. Particle size for the fines was 10 micron maximum with a 5 micron average. Particle size of the grog was varied for different compositions in order to examine the effect of variations of texture. The maximum particle size of grog in any formulation was 48 mesh with a minimum size varying down to 400 mesh. The preponderance of grog in all formulations was in the -65 on 200 mesh range.

Example of Grog Size Used

-48 on 65 mesh	6.46%
-65 on 100 mesh	45.08%
-100 on 200 mesh	32.68%
-200 on 270 mesh	8.24%
-270 on 325 mesh	6.20%
-325 on 400 mesh	1.33%
-400 on pan	negligible

Methocel plus Dextrine were used as binders in the molded formulations. Methocel plus Superloid and Carbowax were used in the extruded formulations. The Carbowax serves as a lubricant.

The firing temperature for all the formulations was 3250°F with a three hour soak.

All the formulations considered in this report were homogeneous, except two which were specially made to be heterogenous. These two were heterogenous because all the stabilizing oxides were added to the grog while the fines were relatively void of stabilizers. After firing, the fines remained predominantly monoclinic, while the grog was stabilized to the cubic form.

TEST METHODS

The tests of this section were conducted by Chance Vought, or for Vought by Southern Research Institute, Birmingham, Alabama.

CVC Conducted Tests

Thermal Shock
Melting Point
Crystal Structure
Flexure and Modulus
Dens ity and Porosity

SRI Conducted Tests

Thermal Expansion
Thermal Conductivity
Emittance
Heat Capacity

Thermal Shock

Thermal shock tests on right circular solid cylinders of the zirconia formulations were conducted with a Thermal Dynamics Model F-40 plasma jet as a heat source. The cylinders were mounted in either low-silica zirconia brick or cement with the face of the cylinder perpendicular to the flame of the jet. Temperatures imposed on the cylinders were measured by a radiation pyrometer, and times were determined by a stop watch. For the determination of heating rates at the elevated temperature ranges, the temperature was raised slowly from room temperature to the test range, the specimen then subjected to the desired heating rate (^{o}F per second), then cooled slowly after the test to prevent greater thermal shock rates being imposed during cool-down. Cylinder condition was examined by using a graphite-soap mixture wiped on the sample surface to indicate cracks. Sufficient tests for each formulation were made either to determine the approximate maximum thermal shock heating rate which could be sustained without failure or to eliminate the particular grade from consideration for the intended application. Failure was defined as surface cracking, spalling, or checking along the sides of the test specimen.

High heat flux was imposed during plasma arc thermal shock tests. Surface temperatures were raised almost instantaneously, creating very high surface thermal gradients. Thermal stress induced by the thermal gradient can cause failure, which is a function of several properties of the ceramic.

An expression for a thermal shock resistance factor, R, has been stated by White (Reference 1) as follows:

$$R = \frac{S_f}{E\alpha}$$

where,

R = a thermal shock resistance factor (thermal gradient through the specimen)

S_f = flexure strength, psi

E = elastic modulus, psi

α = linear coefficient of thermal expansion, in/in/^{o}F

Poisson's ratio is included in a similar expression given by Kingery (Reference 2). It is omitted here inasmuch as it would not change appreciably among the various zirconia formulations.

The term R was calculated for a number of zirconia formulations and compared with experimental thermal shock results.

All data required for the calculation of R were not available for all grades of zirconia. Flexure strength and elastic modulus at room temperature were known in nearly all cases. Elevated temperature mechanical properties were known for two formulations. Estimates were made where data were lacking, following general property versus temperature trends with compensation for density differences among various grades. Estimated values for calculation of the term R are denoted by asterisks.

Thermal Expansion

Thermal expansion measurements were made on cylinders of the zirconia formulations that were 3/4 inch in diameter and 3 inches long. In general, a minimum of eight points on a heating cycle and eight points on a cooling cycle was obtained at temperatures up to 4300^{o}F. These expansion measurements were made in graphite tube dilatometers capable of reliable performance at temperatures to above 5000^{o}F. The dilatometers were self-contained units that were hung in a high temperature furnace.

Contamination of the zirconia test pieces was prevented by wrapping the pieces in tantalum foil and directing a helium purge gas through the dilatometer tube. An inert atmosphere was used in the furnace.

Throughout all runs, careful attention was directed to the indication of inflections in the expansion or contraction of the test pieces. When slope changes were evident, readings were taken much more regularly to insure true analysis of specimen behavior.

Thermal Conductivity

The thermal conductivity was determined with a radial heat flow apparatus that utilized test pieces 1 inch in diameter and 1 inch long with a calorimeter hole drilled axially through the center. The equipment allowed a direct measurement of the thermal conductivity rather than a measurement relative to some standard reference material. A water calorimeter that passes axially through the center of the test piece provided a heat sink at the center of the specimen to create a substantial heat flow through the specimen and to allow the absolute value of the heat flow to be determined. Guards of test materials 1 inch long were placed at both ends of the test piece to maintain a constant radial temperature gradient throughout the entire specimen length and thereby prevent axial heat flow in the specimen. Sight tubes allowed the temperature to be determined at selected points in the test piece either by thermocouples or optical pyrometer. An external heat source was used.

The thermal conductivity values were computed from the relation

$$K = \frac{QL}{TA}$$

where,

Q = heat flow to the calorimeter within the test piece gage section

A = lag mean area for the specimen gage length

T = specimen temperature change across the specimen gage length

L = gage length

Emittance

The emittance of the zirconia formulations was measured by the comparison of the energy received on a 160-junction thermopile from a sample of the material to that received from a black body cavity maintained at the same temperature.

The equipment included an induction heating furnace, a radiometer, and temperature measurement apparatus.

A flat induction heating coil powered by a 25 KW high frequency generator was used to heat tungsten, tantalum, or graphite discs which in turn heated the test pieces.

The radiant energy output from the black body and test pieces was measured by the radiometer.

The cavity-type black body temperatures were determined by using thermocouples placed in the bottom of, or dropped into, the cavity, and by optical pyrometer observations. Specimen temperature was determined by taking the optical temperature of the surface, assuming a grey body distribution of emittance, then calculating emittance from the total radiation and the spectral radiation (optical temperature) values. This calculated emittance was then used to correct the optical temperature. Several runs were made using a thermocouple pressed against the specimen face to provide a check on the optical temperature. Agreement within the limits $\pm 450^{\circ}F$ was obtained.

Heat Capacity

The heat capacity was determined to approximately $4300^{\circ}F$ for only two formulations. This property was not expected to show extremely wide variations between materials. The apparatus employed the drop technique in which the specimen was heated in a furnace with a graphite heating element and then dropped into an ice calorimeter. The ice calorimeter had an ice mantle, which was frozen around the cup. The heat from the specimen was sensed as the change in volume as some of the ice melted and changed into water. The annulus containing the flooded ice mantle communicated with the atmosphere through a mercury column so that the change in volume was read directly on a calibrated glass tube. This provided a volumetric mercury accounting system.

Drops were made at approximately $500^{\circ}F$ increments and enthalpy versus temperature plots were obtained, enthalpy being calculated from the heat removal and the weight of the test piece. The slopes of the enthalpy curves were determined at approximately $500^{\circ}F$ increments, this slope being the average heat capacity of the material at this mean temperature. This method of establishing the heat capacity versus temperature curve has been confirmed to be in close agreement with establishing the heat capacity equation from a least squares fit on a computer.

Accuracy is believed to be within 5% for the method used.

Melting Point

Melting point determinations were made, as in the thermal shock testing, by using a Thermal Dynamics Model F-40 plasma jet as the heat source. Right circular solid cylinders representing the different formulations were

mounted in a low silica zirconia brick, and the plasma flame was directed normal to the cylinder surface. Temperature was observed by optical and radiation pyrometers. Melting was observed by slowly advancing the plasma, in small increments, toward the specimen while viewing with the optical pyrometer. Temperature measurements were made at several points near the melting point. At each reading, as soon as the optical value could be ascertained, a blip was made on the continuously recording radiation pyrometer to correlate the two. Actual melting was rather sharply displayed by the specimen as a brighter spot which would puddle and flow. Usually an area of about 1/4-inch diameter melted. Optical readings were generally repeatable to about $\pm 10^{o}F$. The widest variation was $\pm 30^{o}F$. It is believed that the overall brightness temperature readings are accurate to within $\pm 50^{o}F$. No emittance correction to the optical temperatures were applied because of questionable emittance data above $3000^{o}F$. Relative, rather than absolute, melting point values are reported.

Crystal Structure

The percentages of stabilized cubic zirconia and monoclinic zirconia present in any formulation were determined by x-ray diffraction. Standard mixtures, in weighted proportions, were prepared for monoclinic and cubic phases. The monoclinic standard was prepared by using 99.9% CP Grade zirconium dioxide and determining by x-ray diffraction the amount of background count from the cubic phase. The standard for the cubic phase was prepared by thoroughly mixing 5% CaO with 95% monoclinic standard zirconia and firing at $4250^{o}F$ for at least 4 hours. No monoclinic remained after this firing.

A calibration curve was prepared by using different standard mixtures. Each of the standard mixtures was scanned and the result counted at the analytical points. The plotted results were used for comparison with the x-ray diffraction results from the test pieces.

Flexure and Modulus

The flexure strengths of the materials were determined by stressing the cylinders to failure with a hydraulic universal testing machine. Four point loading of the cylinders was used and the load was applied at a continuous rate of 200 ± 10 points/minute to failure. Modulus was calculated from the associated stress strain curves. Elevated temperature flexure tests were run in the same manner using silicon carbide heating elements to heat the test pieces.

Density and Porosity

Bulk density was measured by the standard ASTM-C-373-56 procedure which is a simple volume-weight determination. Porosity was also measured by the above ASTM procedure, resulting in an apparent porosity (open pores only) obtained from dry, saturated with water, and suspended in water weighings.

Y534 5.62% Lime Stabilized Zirconia, Coarse Grain, Molded
(approximately 11 mole percent lime)

This formulation consists of 30% fines and 70% grog with the following chemical compositions:

	Fines	Grog
ZrO_2	93.60	93.70
CaO	5.68	5.60
SiO_2	0.06	0.06
MgO	0.60	0.60
$CaSO_4$	0.02+	--
SO_4	0.02	--

There is no thermal shock data on this material. A quantitative indication of its ability to withstand thermal shock is derived from the expression as discussed on page 5 . The resistance factor obtained for any temperature may be compared to that factor (at the same temperature) of a tested material. The higher value supposedly indicates the material that has the best thermal shock resistance for the temperature taken.

Temp, °F	E	S_F	R
RT	4.0*	8200*	568
1000	3.7*	6000*	299
1500	2.7*	5750*	339
2000	1.5*	4800*	510
2500	0.5*	1000*	370
3000	0.3*	400*	303
3500	0.3*	400*	undefined
4000	0.3*	400*	undefined

Flexure strength and modulus data that are marked with an asterisk (*) are not derived from tests, but were obtained from curves plotted from measured data.

Undefined resistance factors are due to physical properties such as crystal inversions that are not independent of temperature.

Density = 0. 154 lb/in^3

Porosity = 22. 40%

Melting Point Data - Table 25

Crystal Structure Data - Table 26

Temperature-Time History of Thermal Expansions for this and all other materials are shown in Table 27.

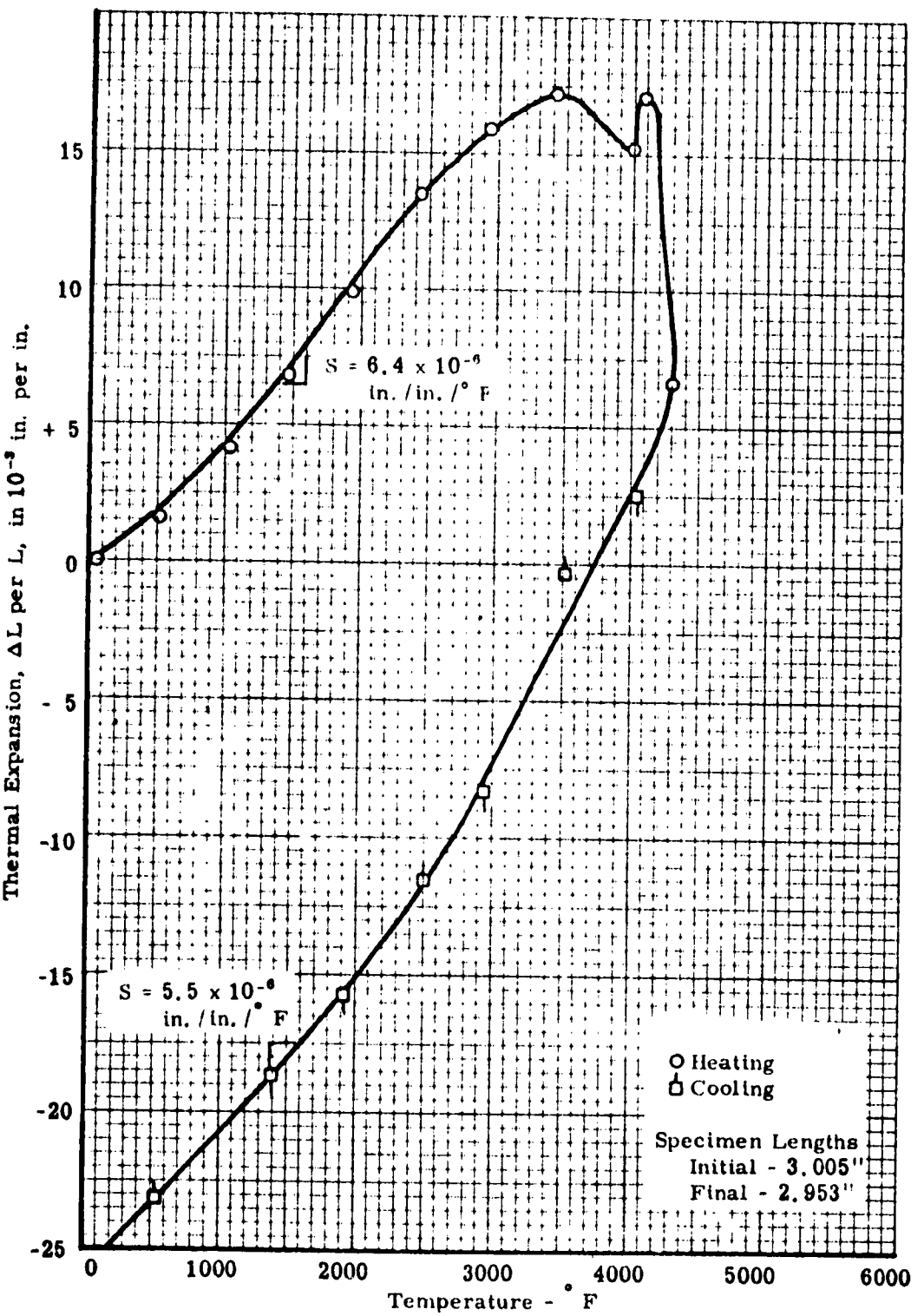


Figure 1 Thermal Expansion of Zirconia, 5.62% CaO, Coarse Grain, Molded.

Table 1

Thermal Expansion of Zirconia 5.62% CaO, Coarse Grain, Molded.

Temperature °F	Observed Total Elongation 10^{-3} inches	Observed Unit Elongation 10^{-3} inches/inch	Unit Elongation Correction for Dilatometer Motion 10^{-3} inches/inch	Corrected Specimen Unit Elongation 10^{-3} inches/inch
62	0	0	0	0
511	3.8	1.3	0.4	1.7
1022	10.6	3.5	0.8	4.3
1488	17.3	5.8	1.2	7.0
1950	24.8	8.3	1.7	10.0
2430	33.5	11.2	2.3	13.5
2960	39.1	13.0	3.0	16.0
3440	40.5	13.5	3.8	17.3
4020	32.0	10.7	4.7	15.4
4100	37.0	12.3	4.9	17.2
4310	4.0	1.3	5.3	6.6
4050	- 7.0	- 2.3	4.8	2.5
3525	-13.0	- 4.3	4.0	- 0.3
2975	-33.5	-11.2	3.0	- 8.2
2500	-42.1	-14.0	2.5	-11.5
1925	-52.0	-17.3	1.7	-15.6
1400	-59.5	-19.8	1.1	-18.7
998	-64.6	-21.5	0.8	-20.7
523	-70.9	-23.6	0.4	-23.2
65	-76.5	-25.5	0	-25.5

Initial Specimen Length = 3.005"
Final Specimen Length = 2.953"

Y544 3% Lime Stabilized Zirconia, Fine Grain, Molded
(approximately 6-1/2 mole percent lime)

This formulation consists of 100% fines with the following chemical composition:

ZrO_2	96.00
CaO	2.99
SiO2	0.34
MgO	0.21
$CaSO_4$	0.26
SO_4	0.18

There is no thermal shock data on this material.

A quantitative measure of thermal shock, flexure strength, and modulus of elasticity vs. temperature is as follows:

Temp, °F	S_f	E	R
RT	38000*	17.0*	568
1000	28000*	16.0*	314
1500	21200*	13.5*	305
2000	18000*	2.0*	1700
2500	1200*	0.6*	455
3000	400*	0.3*	245
3500	400*	0.3*	256
4000	400*	0.3*	275

As expected, the fine grain material has considerably more strength than those materials with some percentage of grog. This strength falls off rapidly with the higher temperatures as may be observed in this and the following material. In the 2000°F range, the formulation above is very resistant to thermal shock, yet in the 3000°F range it has relatively poor thermal shock resistance when compared to the other zirconia materials of this report.

The room temperature flexure strength of this material was taken from a plot of density vs. flexure strength for a number of materials tested. The curve was extrapolated considerably (due to the high measured density) in order to obtain a strength value. It is doubtful that this value is as high as indicated.

It may be noted here that as the percent fines are increased in any formulation, the porosity is decreased.

Density = 0.203 lb/in^3

Porosity = 0.53%

Melting Point Data - Table 25

Crystal Structure Data - Table 26

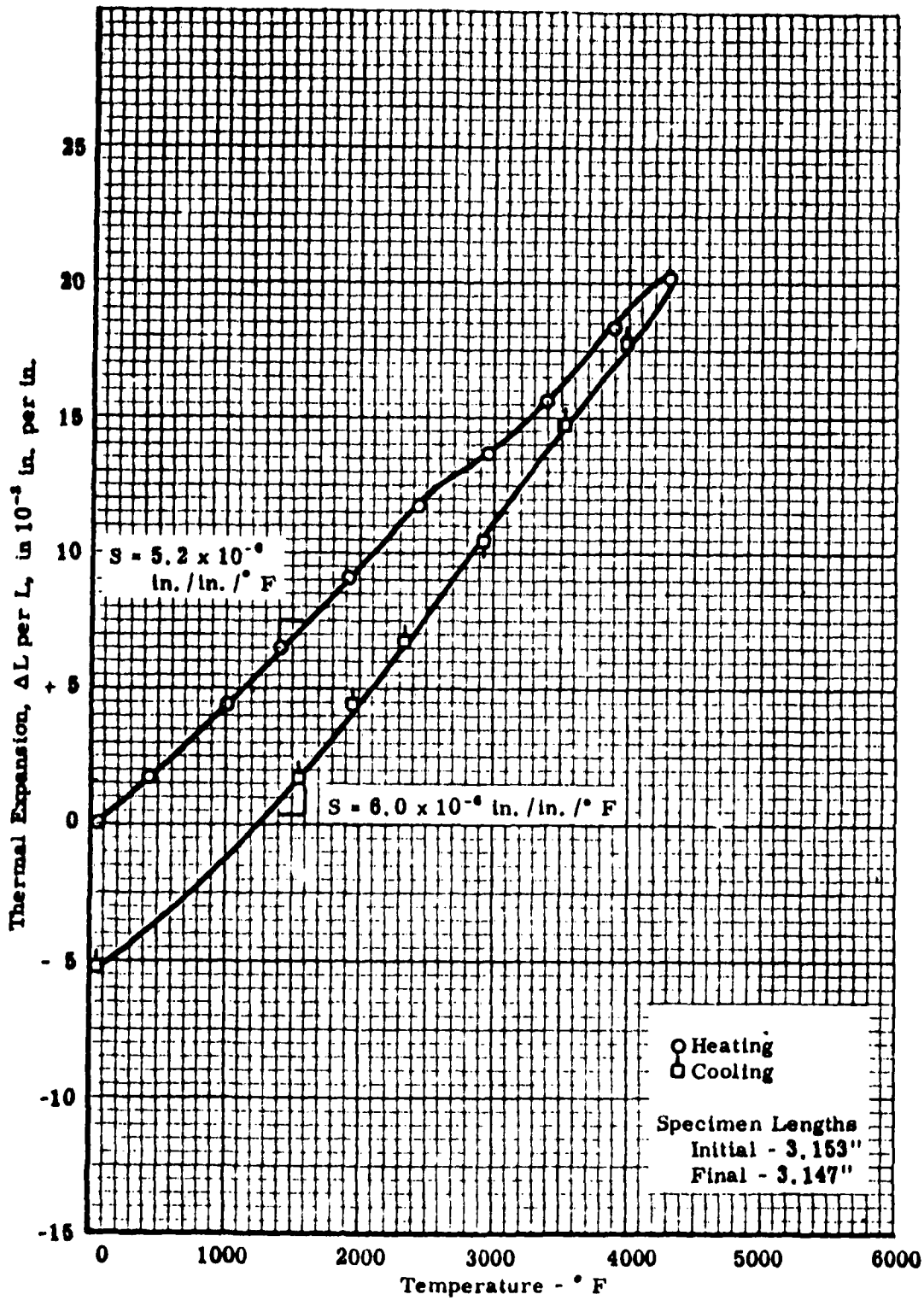


Figure 2. Thermal Expansion of Zirconia, 3% CaO, Fine Grain, Molded.

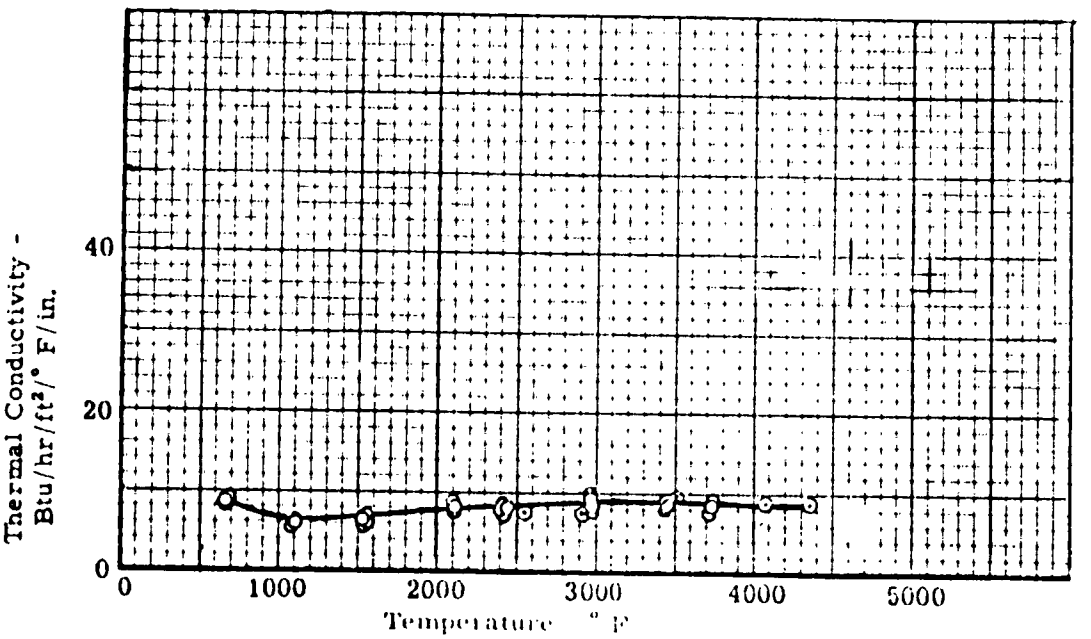


Figure 3 Thermal Conductivity of Zirconia, 3% CaO, Fine Texture Molded

Table 2

Thermal Expansion of Zirconia, 3% CaO, Fine Grain, Molded

Temperature °F	Observed Total Elongation 10^{-3} inches	Observed Unit Elongation 10^{-3} inches/inch	Unit Elongation Correction for Dilatometer Motion 10^{-3} inches/inch	Corrected Specimen Unit Elongation 10^{-3} inches/inch
73	0	0	0	0
448	4.6	1.4	0.2	1.6
1005	11.7	3.7	0.7	4.4
1418	17.0	5.4	1.1	6.5
1910	23.1	7.3	1.7	9.0
2450	29.7	9.3	2.4	11.7
2970	33.1	10.5	3.1	13.6
3415	37.0	11.7	3.9	15.6
3940	43.1	13.7	4.7	18.4
4325	47.4	15.0	5.3	20.3
4000	41.2	13.1	4.8	17.9
3550	33.5	10.6	4.0	14.6
2960	22.9	7.3	3.2	10.5
2350	13.4	4.3	2.3	6.6
1980	8.7	2.8	1.7	4.5
1550	1.9	0.6	1.1	1.7
70	-16.4	- 5.2	0	- 5.2

Initial Specimen Length = 3.153"
Final Specimen Length = 3.147"

Table 3

Thermal Conductivity of Zirconia, 3% CaO, Fine Grain, Molded

Spec. Outer Face Temp. °F	ΔT Across Test Section °F	Radial Heat Flow Through ½" Calorimeter Section, BTU/Hr.	Mean Temp. of Test Section, °F	Thermal Conductivity of Test Section BTU/Hr/Ft²/°F/Inch
-	207	29.4	667	8.10
-	208	31.4	680	8.60
-	205	30.6	702	8.51
-	201	32.4	711	9.19
-	199	30.0	718	8.60
-	368	35.5	1083	5.51
-	369	37.3	1086	5.77
-	376	43.7	1105	6.64
-	599	52.6	1561	5.01
-	601	62.5	1568	5.93
-	604	70.2	1575	6.63
-	605	68.4	1579	6.44
2640	700	85.2	2102	6.95
2640	690	89.9	2110	7.43
2640	690	85.9	2110	7.09
2640	690	110.0	2110	9.10
3040	800	92.1	2425	6.56
3040	800	92.8	2425	6.60
3040	800	92.5	2425	6.59
3035	800	106.0	2420	7.55
3035	800	118.0	2420	8.40
3600	810	92.8	2978	6.53
3600	810	120.0	2978	8.48
3600	810	136.0	2978	9.56
3640	830	140.0	3002	9.85
3640	840	153.0	2995	10.75
4120	930	112.0	3406	6.86
4120	930	140.0	3406	8.58
4180	960	152.0	3441	9.02
4180	960	155.0	3441	9.20
4500	1020	147.0	3716	8.21
4500	1020	141.0	3716	7.87
4500	1060	152.0	3686	8.17
4500	1060	165.0	3686	8.86

Y237 3% Lime Stabilized Zirconia, Fine Grain, Extruded
(approximately 3-1/2 mole percent lime)

This formulation is the same as the preceding one, except that test pieces were extruded rather than molded.

This material failed in thermal shock at 62°F/sec. The maximum thermal shock the material will withstand in the 2000° to 3000°F range is somewhere below this level. Tests were not run to establish this value. The quantitative measure of thermal shock as shown below indicates that the failure most likely occurred when the temperature approached the 3000°F point.

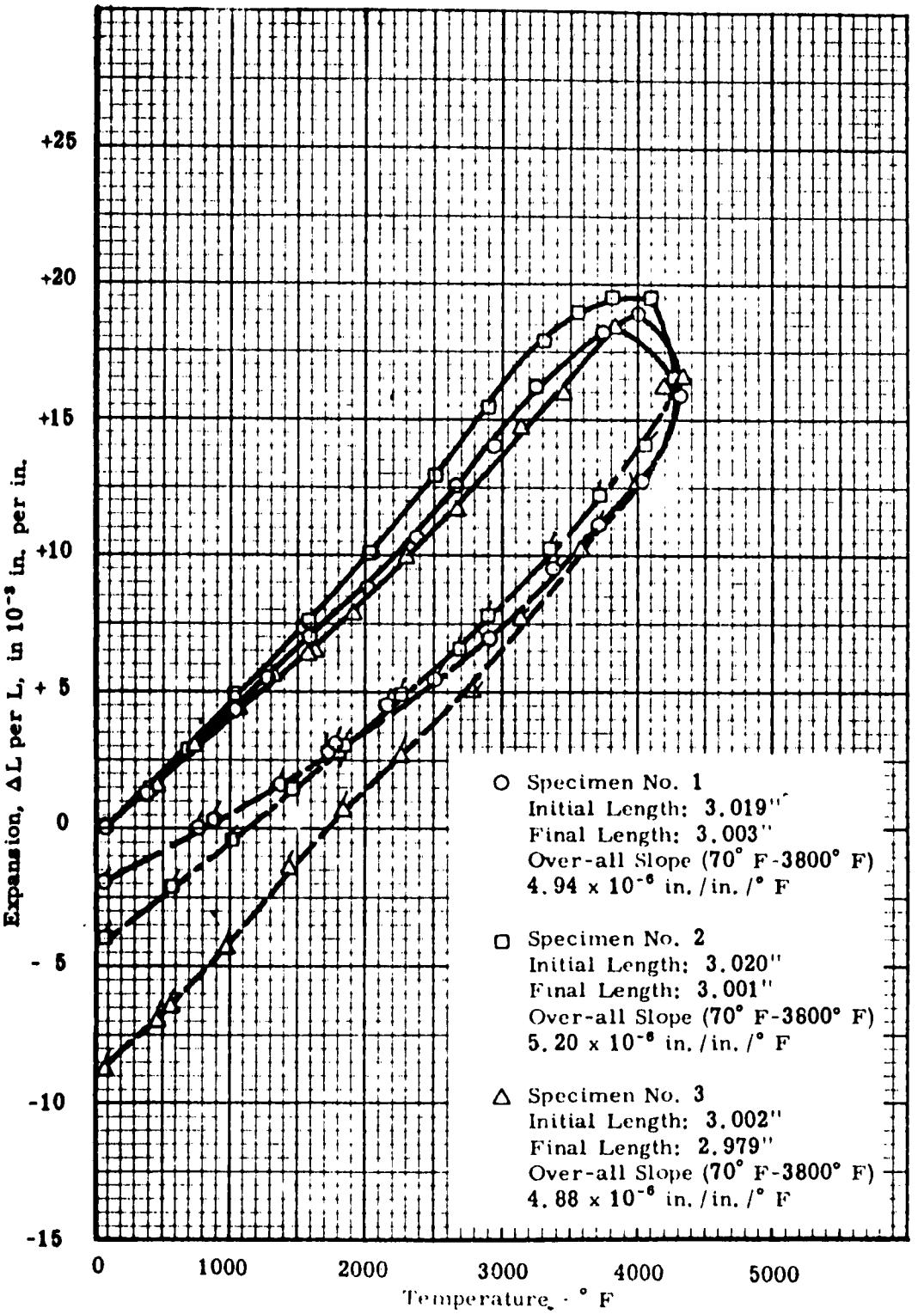
Temp, °F	S_f	E	R
RT	31,372	13.3	590
1000	28,000*	12.1*	432
1500	18,500*	9.8*	418
2000	16,200*	2.0*	1723
2500	1,200*	0.6*	350
3000	400*	0.3*	234
3500	400*	0.3*	296
4000	400*	0.3*	undefined

Density = 0.194 lb/in^3

Porosity = 0.43%

Melting Point Data - Table 25

Crystal Structure Data - Table 26



Figure, 4 Thermal Expansion of 3% Lime Stabilized Zirconia, Fine Grain, Extruded

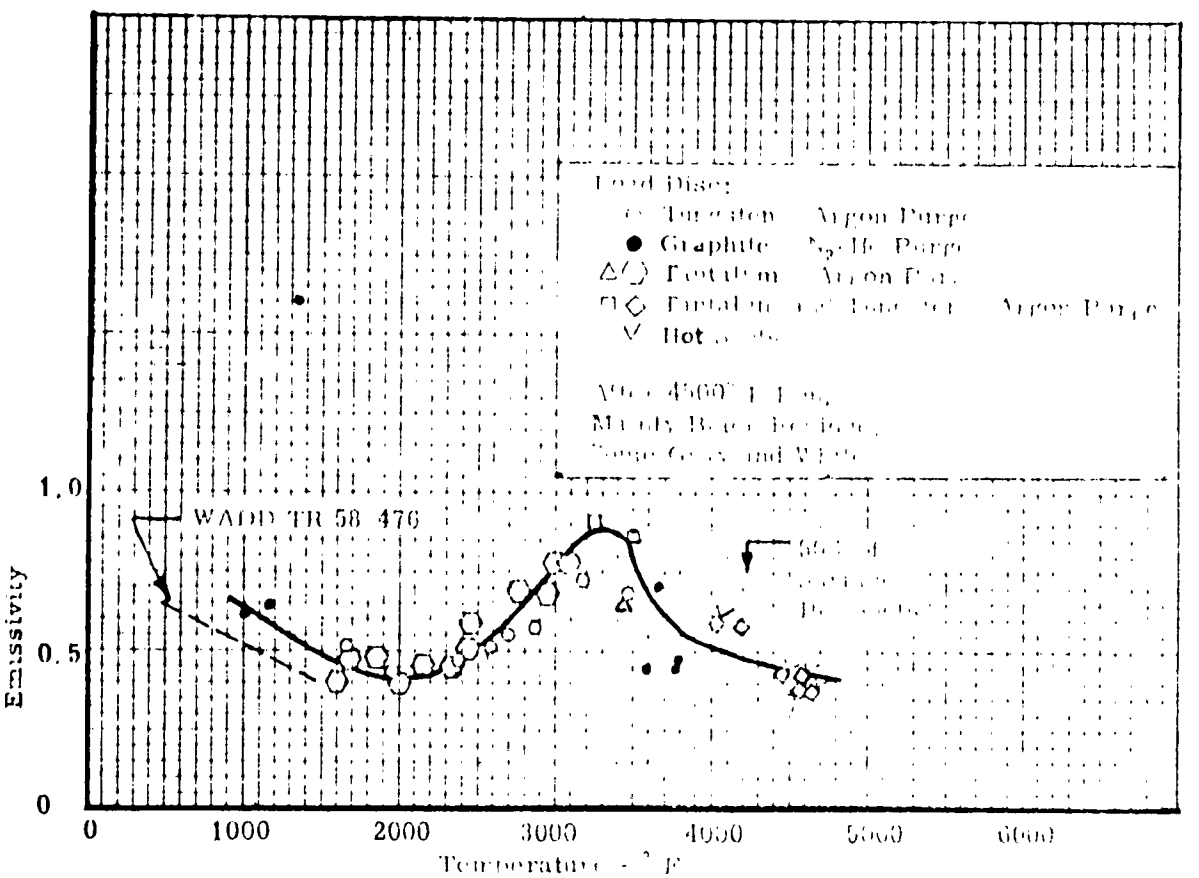
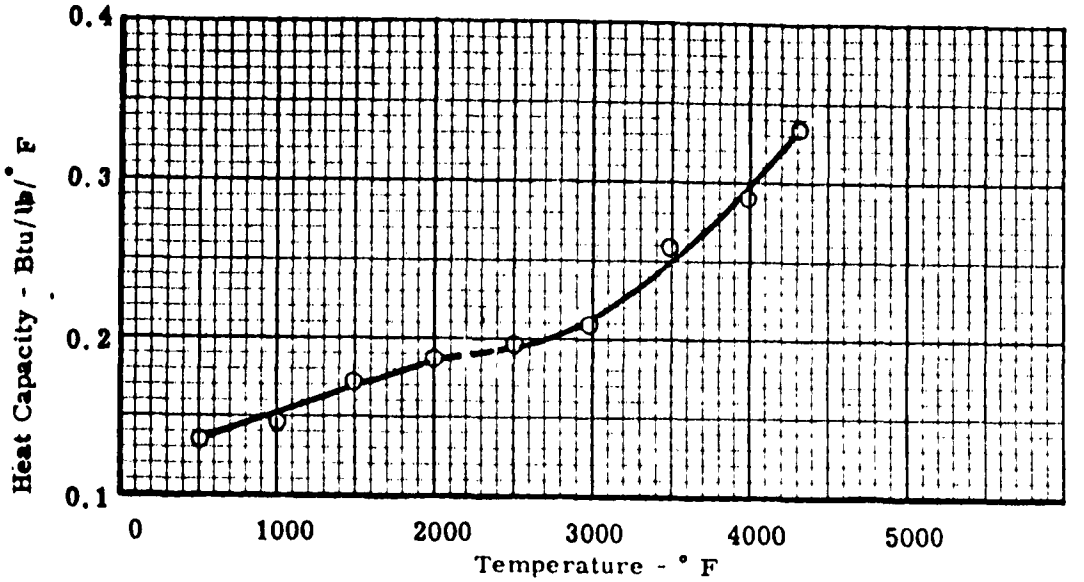


Figure 5 Total Normal Emittance of Zirconia [illegible] CaO, Large Grain Extruded



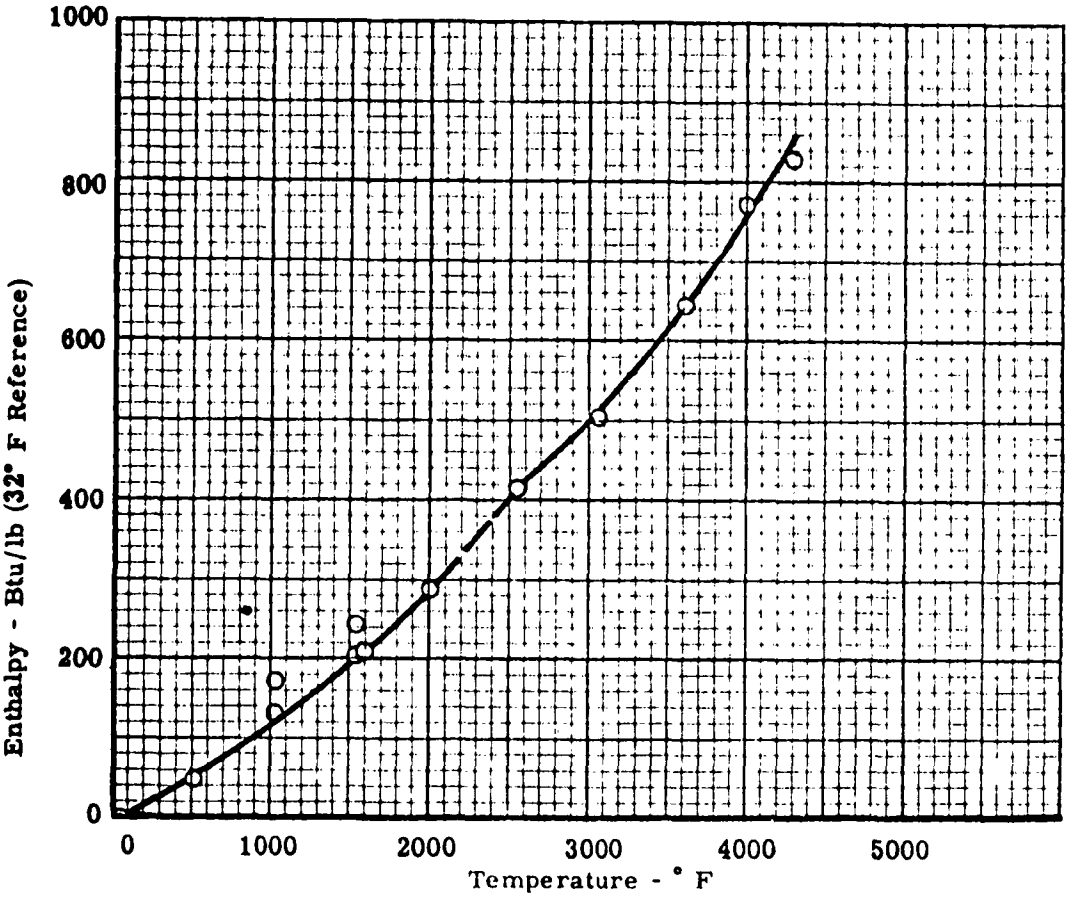
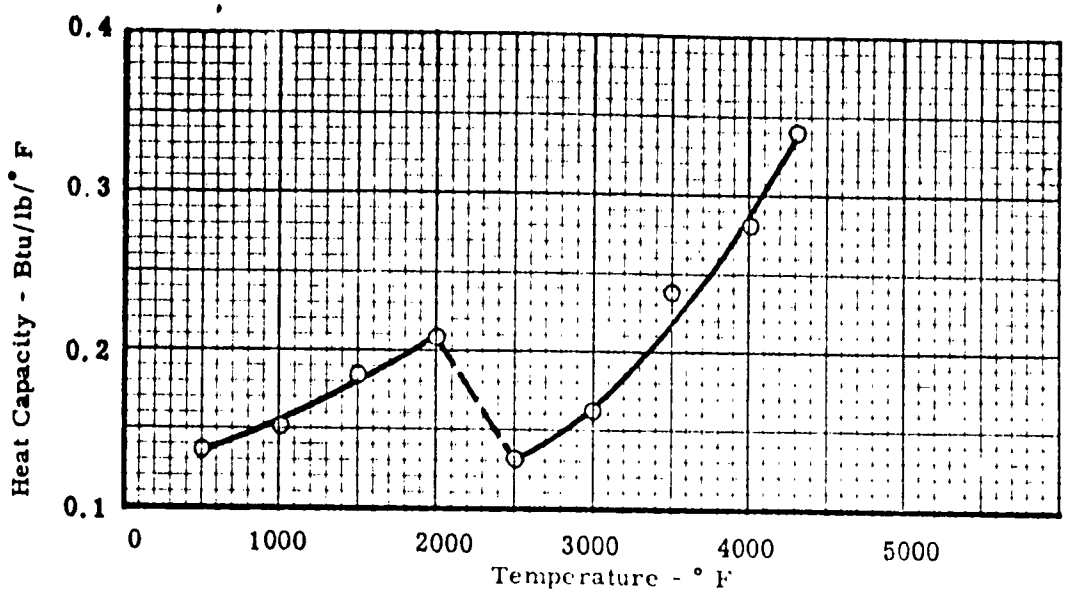


Figure 6A Enthalpy and Heat Capacity for No.1 Specimen of 3% Lime Stabilized Zirconia, Fine Grain, Extruded.



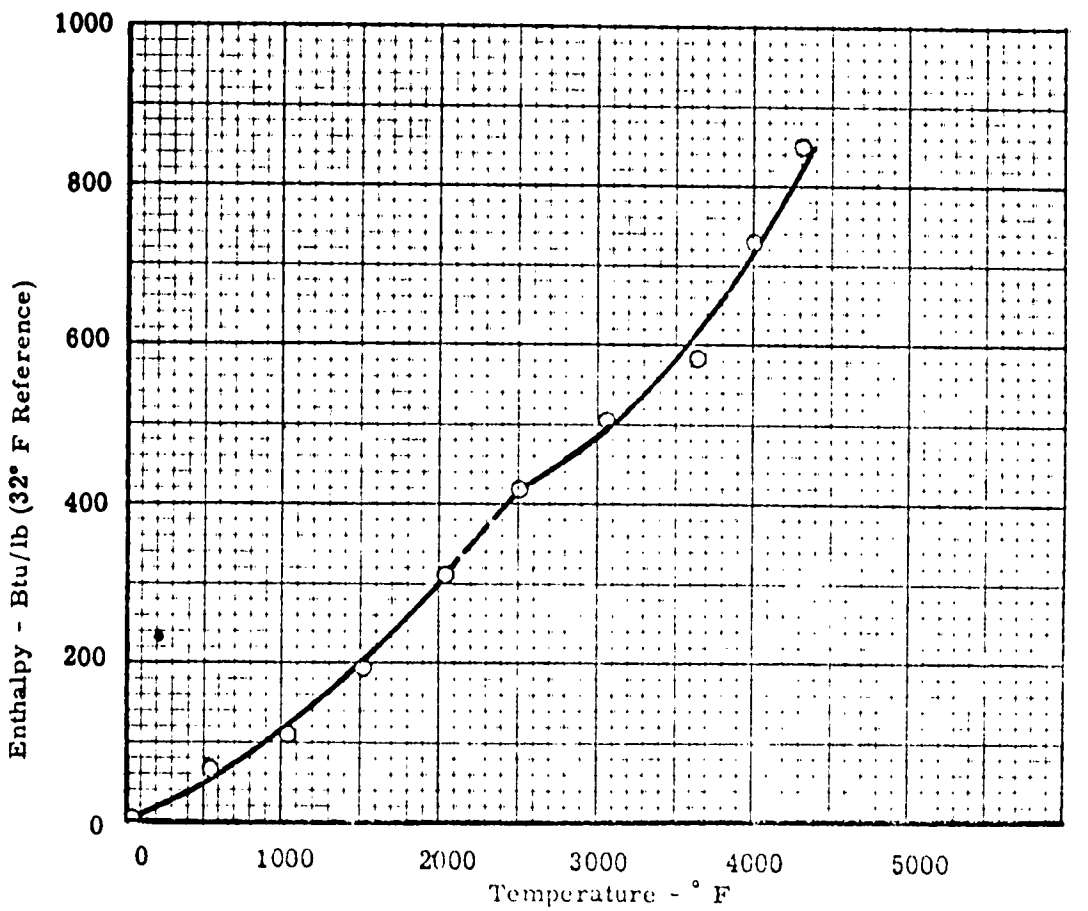
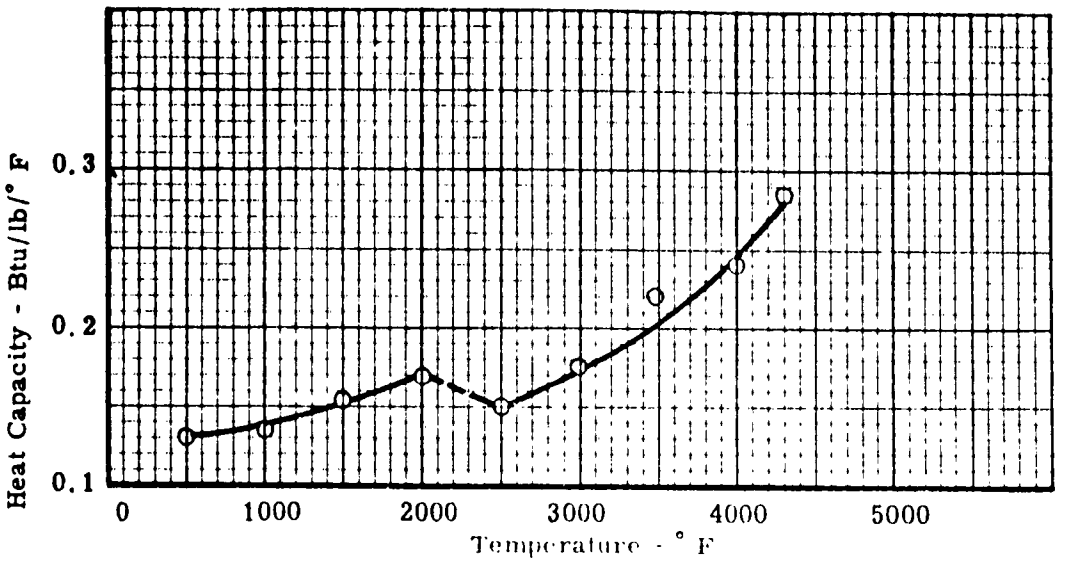


Figure 6B Enthalpy and Heat Capacity for No. 2 Specimen of 3% Lime Stabilized Zirconia, Fine Grain, Extruded.



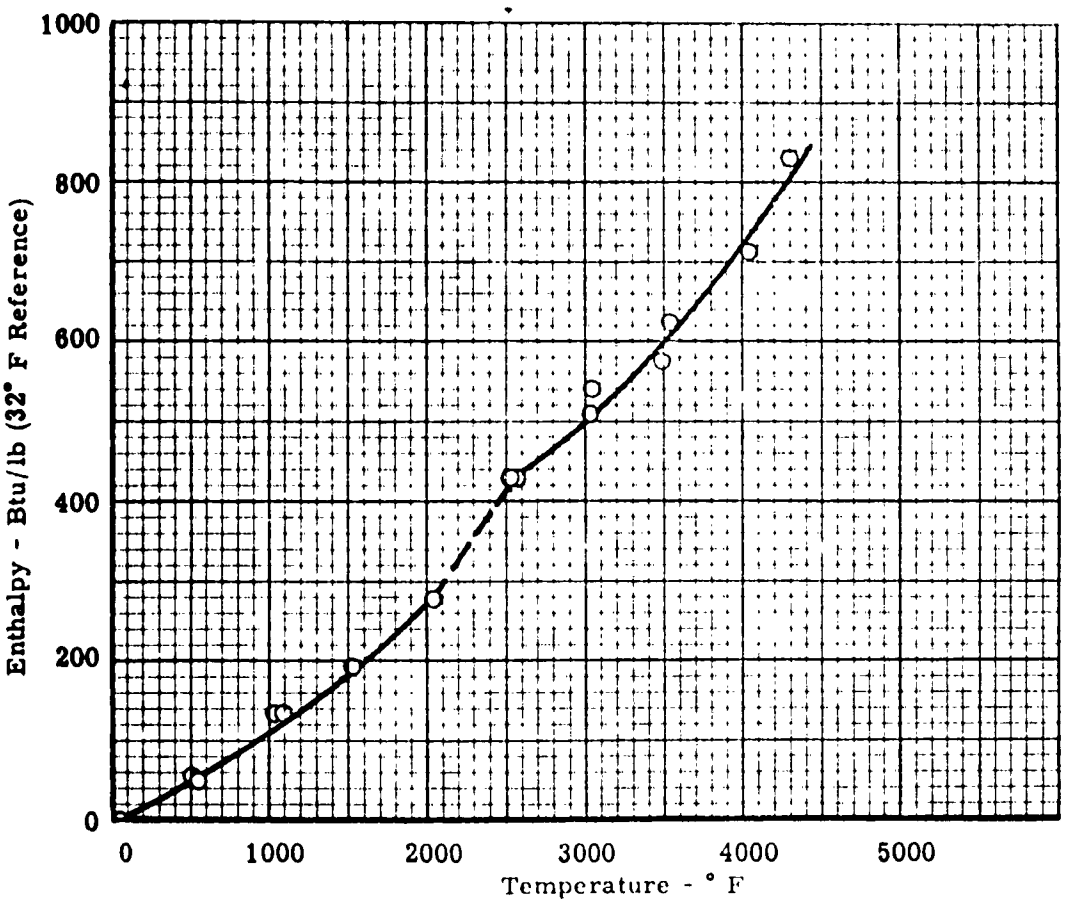


Figure 6C Enthalpy and Heat Capacity for No.3 Specimen of 3% Lime Stabilized Zirconia, Fine Grain, Extruded.

Table 4

Temperature Data for Zirconia, 3% CaO, Fine Grain

Thermocouple Temperature °F	Observed Optical Temperature °F	Optical Temperature Corrected for Emissivity °F	Elapse of Time from Start of Run Hrs Mins	Radiometer Output Millivolts
	3910	4160	0-09	4.20
	4100	4550		4.20
	4050	4550		3.81
	3780	4010		3.75
	4000	4425		3.90
	4100	4620	0-16	3.75
	3210	3230		2.668
	3430	3490		3.260
	3280	3430		2.278
	1490	1580	0-05	0.095
	1600	1665	0-11	0.135
	1760	1850	0-16	0.185
	2030	2150	0-20	0.311
	2180	2320		0.390
	2270	2400		0.510
	2310	2410	0-27	0.597
	2650	2730		1.126
	2830	2730		1.410
	2700	2960		1.633
	2980	3050	0-40	1.792
	1550	1610	0-05	0.133
	2200	2340	0-11	0.426
	1840	1950	0-19	0.212
	1650	1730	0-21	0.155
	1850	1940	0-25	0.246
	2100	2200	0-32	0.393
	2430	2570	0-38	0.649
	2530	2670	0-45	0.793
	2700	2840		1.052
	3050	3150		1.90
	3300	3430	0-53	2.44

Table 4 (Continued)

Temperature Data for Zirconia, 3% CaO, Fine Grain

Thermocouple Temperature °F	Observed Optical Temperature °F	Optical Temperature Corrected for Emissivity °F	Elapse of Time from Start of Run Hrs Mins	Radiometer Output Millivolts
	2000	2080	0-05	0.341
	3270	3570		1.799
	3430	3760	0-22	2.185
	3430	3760	0-27	2.198
833				0.026
1035				0.048
1168				0.068

Y842 2.17% Lime Stabilized Zirconia, Coarse Grain Molded (approximately 4-1/2 mole percent lime)

This formulation consists of 30% fines and 70% grog with the following chemical compositions:

	Fines	Grog
ZrO_2	96.00	97.60
CaO	2.99	1.82
SiO_2	0.34	0.12
MgO	0.21	--
$CaSO_4$	0.26	0.27
SO_4	0.18	0.17

The thermal shock data (Figure 31) shows that this material is very resistant to thermal shock over a range from room temperature to 4000°F, withstanding 1300°F/sec. The quantitative measure of thermal shock shows that this formulation is one of the best thermal shock resistors at temperatures exceeding 3000°F. This material, as in the one following, has low strength at room temperature, accounting for the low thermal shock resistance factor.

Temp °F	S_f	E	R
RT	2500	2.5	206
1000	2200*	2.1*	223
1500	1900*	1.9*	244
2000	1800*	1.4*	212
2500	500*	0.3*	245
3000	400*	0.3*	280
3500	400*	0.3*	500+
4000	400*	0.3*	--

Density = 0.168 lb/in^3

Porosity = 18.58%

Melting Point Data - Table 25

Crystal Structure Data - Table 26

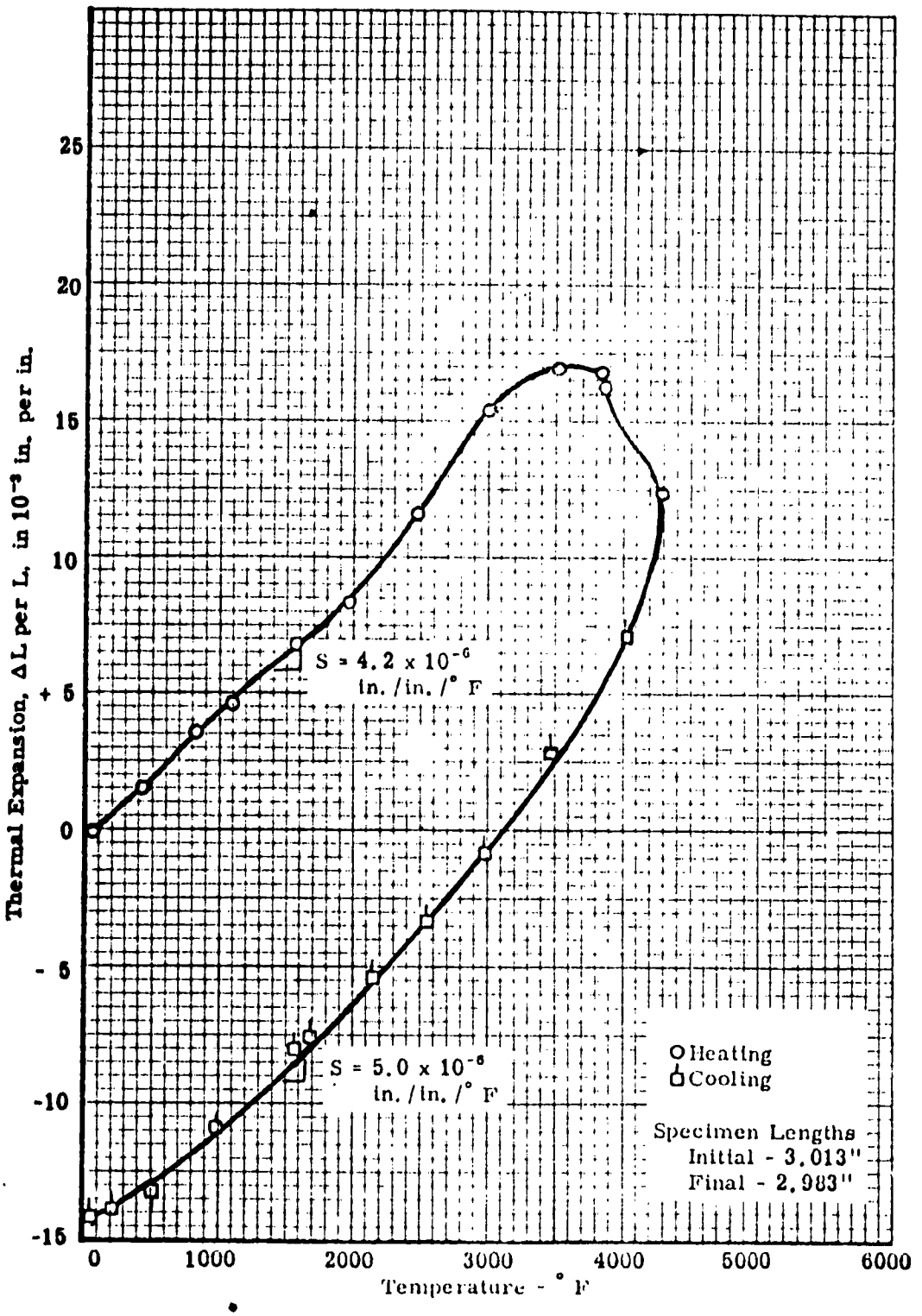


Figure 7 Thermal Expansion of Zirconia, 2.17 % CaO, Coarse Grain, Molded.

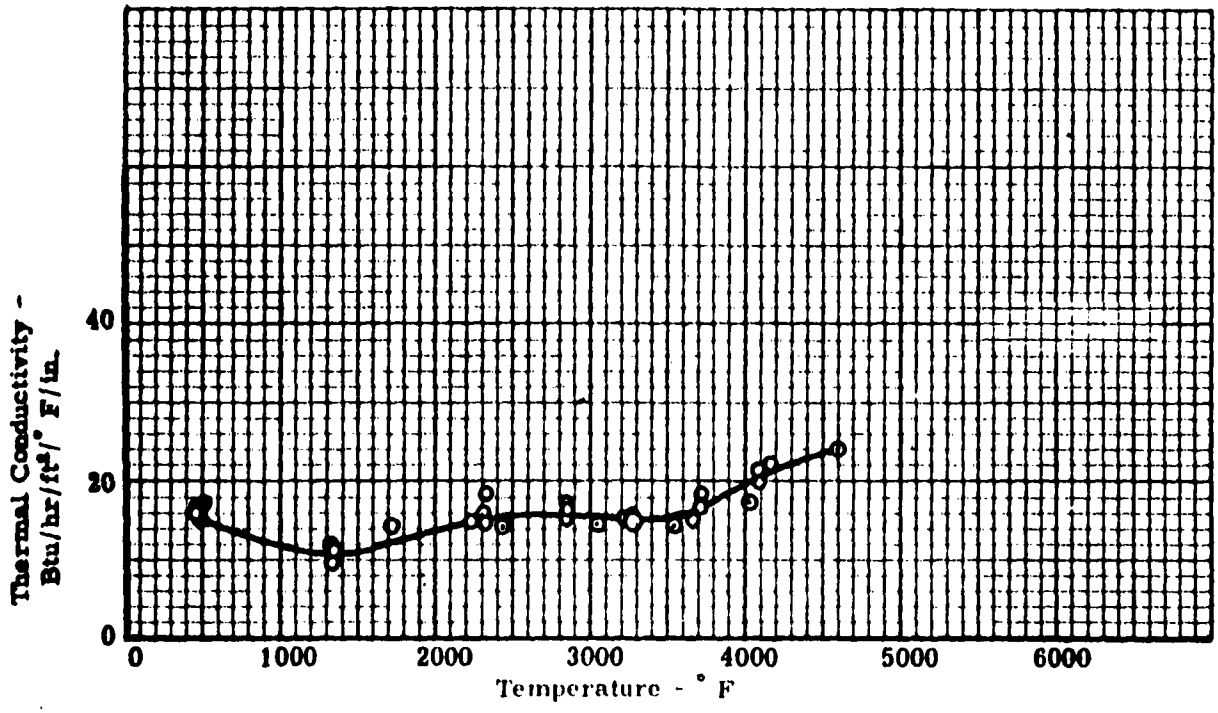


Figure 8 Thermal Conductivity of Stabilized Zirconia, 2.17% CaO, Coarse Molded, Standard Porosity.

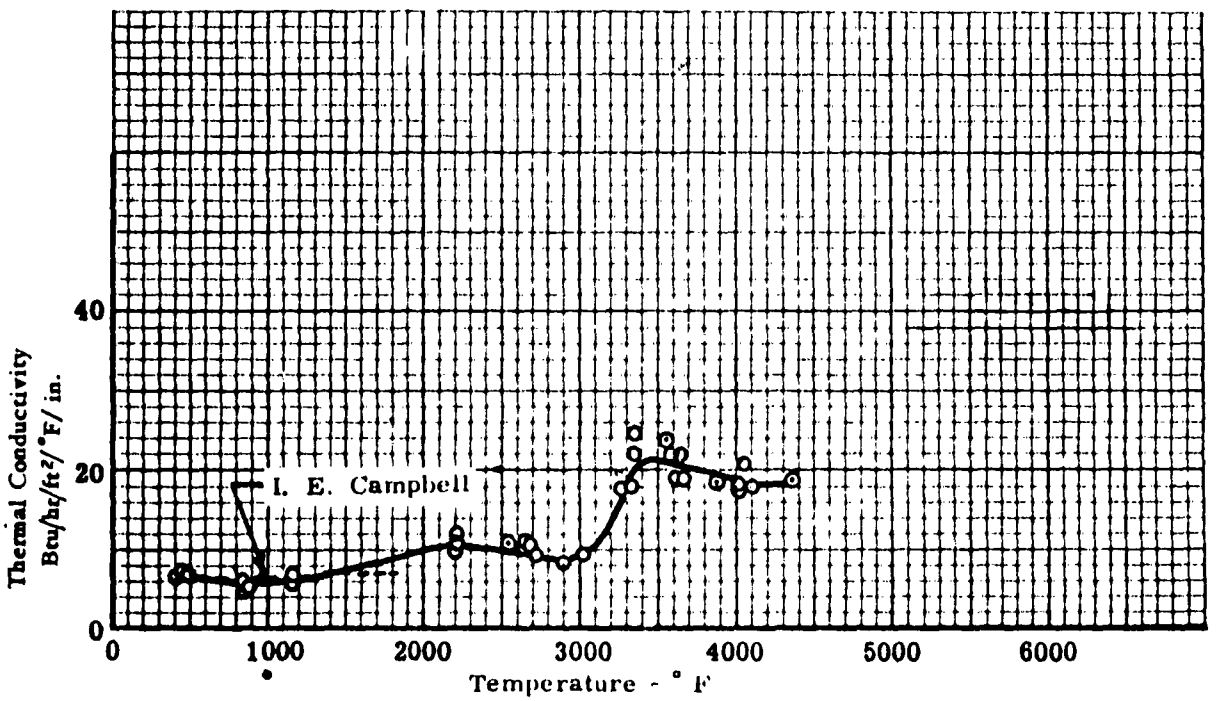


Figure 9 Thermal Conductivity of Stabilized Zirconia, 2.17% CaO, Coarse Grain, Molded, 25% Porosity.

Table 5

Thermal Expansion of Zirconia, 2.17% CaO, Coarse Grain, Molded

Temperature ° F	Observed Total Elongation 10^{-3} inches	Observed Unit Elongation 10^{-3} inches/inch	Unit Elongation Correction for Dilatometer Motion 10^{-3} inches/inch	Corrected Specimen Unit Elongation 10^{-3} inches/inch
79	0	0	0	0
430	4.2	1.4	0.2	1.6
837	9.2	3.1	0.5	3.6
1089	12.0	4.0	0.8	4.8
1584	16.7	5.5	1.3	6.8
1590	16.9	5.6	1.3	6.9
1975	20.5	6.7	1.8	8.5
2490	28.0	9.3	2.4	11.7
3000	36.7	12.2	3.2	15.4
3510	39.2	13.0	4.0	17.0
3860	37.2	12.4	4.5	16.9
3880	35.6	11.8	4.6	16.4
4300	22.0	7.3	5.3	12.6
4030	6.7	2.4	4.8	7.2
3500	- 3.0	- 1.0	4.0	3.0
3005	-11.6	- 3.9	3.2	- 0.7
2570	-17.1	- 5.7	2.5	- 3.2
2140	-21.9	- 7.3	2.0	- 5.3
1700	-26.9	- 8.9	1.4	- 7.5
1543	-27.4	- 9.1	1.2	- 7.9
1003	-34.2	-11.4	0.7	-10.7
517	-40.2	-13.4	0.3	-13.1
197	-41.6	-13.8	0.1	-13.7
66	-42.1	-14.0	0	-14.0

Initial Specimen Length = 3.013"
Final Specimen Length = 2.983"

Table 6

Thermal Conductivity of Stabilized Zirconia, 2.17% CaO
Coarse Grain, Molded, Standard Porosity

Spec. Outer Face Temp. ° F	ΔT Across Test Section ° F	Radial Heat Flow Through $\frac{1}{4}$" Calorimeter Section $\frac{BTU}{Hr.}$	Mean Temp. of Test Section, ° F	Thermal Conductivity of Test Section BTU/Hr/Ft²/°F/Inch
-	471	97.6	1310	11.8
-	450	78.2	1316	9.90
-	443	85.2	1320	10.95
-	432	73.0	1322	9.64
-	177	48.4	487	15.6
-	180	58.5	492	18.5
-	181	52.0	494	16.4
-	181	54.3	494	17.1
-	381	146.5	1020	21.9
-	398	114.7	1035	16.4
-	399	80.0	1038	11.4
-	410	152.7	1046	21.2
2510	460	115.0	2243	14.25
2550	405	107.8	2317	18.2
2560	415	106.8	2321	14.7
2570	425	124.0	2325	16.7
3150	510	154.0	2856	17.2
3160	530	137.5	2854	14.8
3170	530	148.0	2864	15.9
3185	580	164.3	2851	16.16
3660	705	198.0	3253	16.0
3670	660	170.3	3290	14.8
3680	720	186.5	3265	20.1
3695	720	186.2	3280	14.8
4140	730	233.0	3718	24.8
4170	785	226.0	3718	16.5
4145	830	221.0	3667	15.2
4160	880	236.0	3653	15.3
4780	1200	457.0	4088	21.7
4800	1225	424.0	4094	19.7
4760	1045	402.0	4158	22.0
4740	1020	400.0	4152	22.4

Table 7

Thermal Conductivity of Stabilized Zirconia, 2.17% CaO
Coarse Grain, Molded, 25% Porosity

Spec. Outer Face Temp. ° F	ΔT Across Test Section ° F	Radial Heat Flow Through $\frac{1}{4}$" Calorimeter Section $\frac{BTU}{Hr.}$	Mean Temp. of Test Section, ° F	Thermal Conductivity of Test Section BTU/Hr/Ft^2/°F/Inch
-	163	19.5	485	6.82
-	163	20.0	488	7.00
-	164	20.5	497	7.12
-	338	35.0	885	5.90
-	338	33.9	891	5.72
-	337	32.5	902	5.50
-	463	57.4	1168	7.06
-	458	46.7	1178	5.80
-	458	58.0	1185	7.22
-	451	46.7	1198	5.81
2600	665	112.7	2216	9.67
2640	700	130.0	2237	10.6
2660	780	153.0	2210	11.2
2660	795	140.0	2202	10.05
3200	995	185.0	2626	10.6
3270	1030	198.0	2676	10.9
3310	1040	190.0	2710	10.4
3310	995	156.0	2736	8.94
3600	540	164.8	3290	17.4
3620	495	150.0	3336	17.3
3650	465	180.0	3383	22.1
3930	500	192.6	3642	21.9
3960	520	180.7	3660	19.8
3990	520	172.0	3690	18.85
3980	500	163.0	3692	18.6
4410	660	212.0	4030	18.3
4390	610	189.5	4038	17.7
4450	585	186.0	4113	18.1
4420	595	213.5	4077	20.4

Y481 2.17% Lime Stabilized Zirconia, Coarse Grain, Extruded
(approximately 4-1/2 mole percent lime)

This formulation is the same as the preceding one, except test pieces were extruded rather than molded.

Thermal shock data on this material shows that 185°F/sec is the maximum thermal shock that it will withstand. The same material with larger mesh grog imparted more thermal shock resistance as indicated to be as high as 500°F/sec. (Figure 31). It may also be noted by this formulation (Figure 13) that the size of the thermal shock test piece makes a difference in the shock resistance. The larger test piece will have less resistance, the temperature difference through the material being of greater magnitude. J. White (Reference 1) states that if cylinders of the same material, but with different dimensions are tested at a constant value of heat-transfer coefficient, the temperature difference to cause failure should be inversely proportional to the radius of the cylinder.

Temp °F	S_f	E	R
RT	7800	10.6	167
1000 •	5200	9.3	125
1500	4800	6.7	149
2000	2900	1.6	334
2500	700	1.0	125
3000	400	0.3	266
3500	400*	0.3*	333
4000	400*	0.3*	undefined

This material shows that the method of forming has a definite effect on the modulus when compared to the preceding material. The extruded formulation has the higher expansion coefficient. Its forming pressure is lower (1000 psi vs. 5000 psi), but the expansion was measured parallel to the direction of extrusion. A small degree of an anisotropy may exist due to extrusion.

Density = 0.165 lb/in^3

Porosity = 19.4%

Y601 Larger Mesh Grog

Density = 0.1617 lb/in^3

Porosity = 27.2%

Melting Point Data - Table 25

Crystal Structure - Table 26

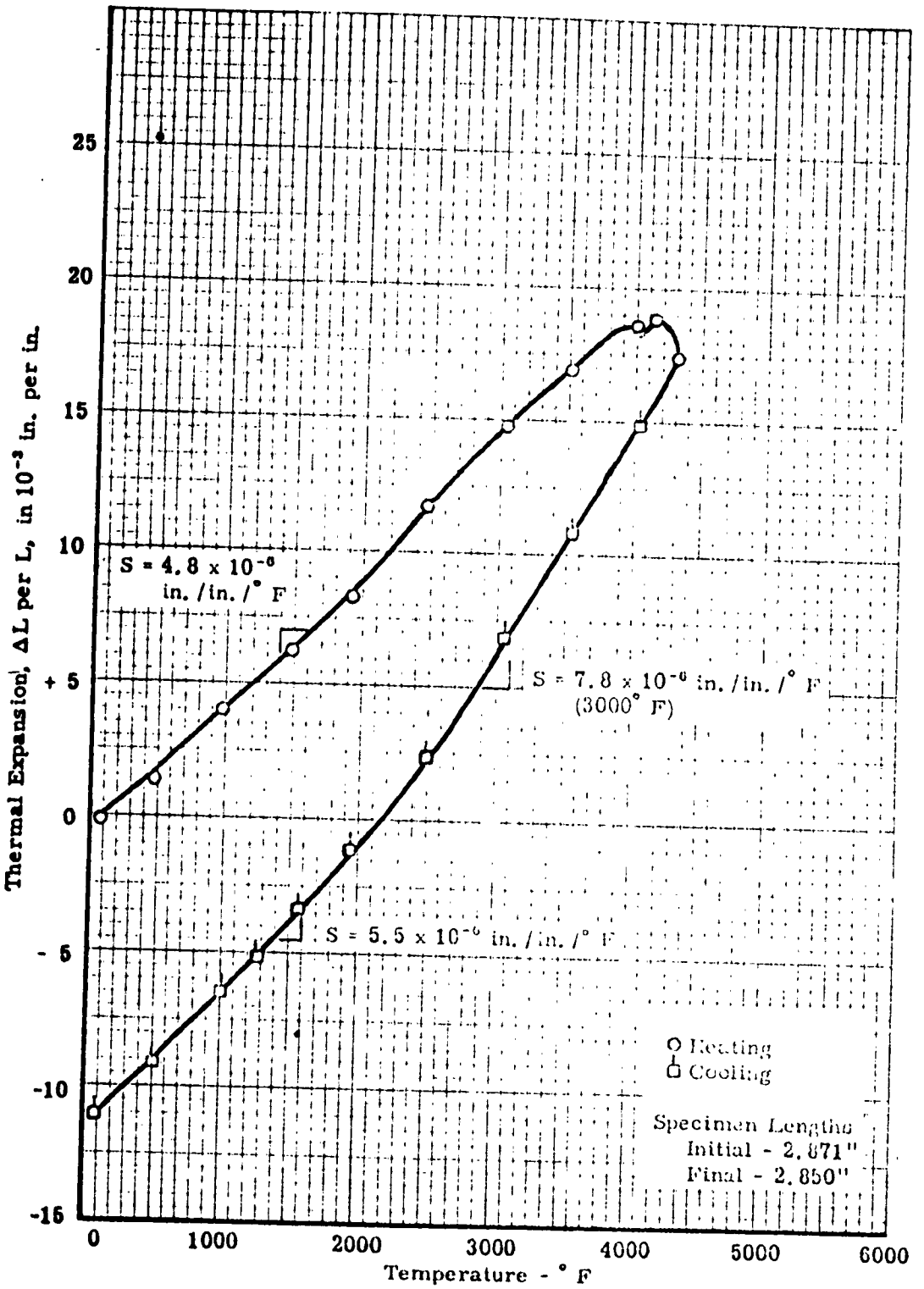


Figure 10 Thermal Expansion of Zirconia, 2.17 % CaO, Coarse Grain, Extruded.

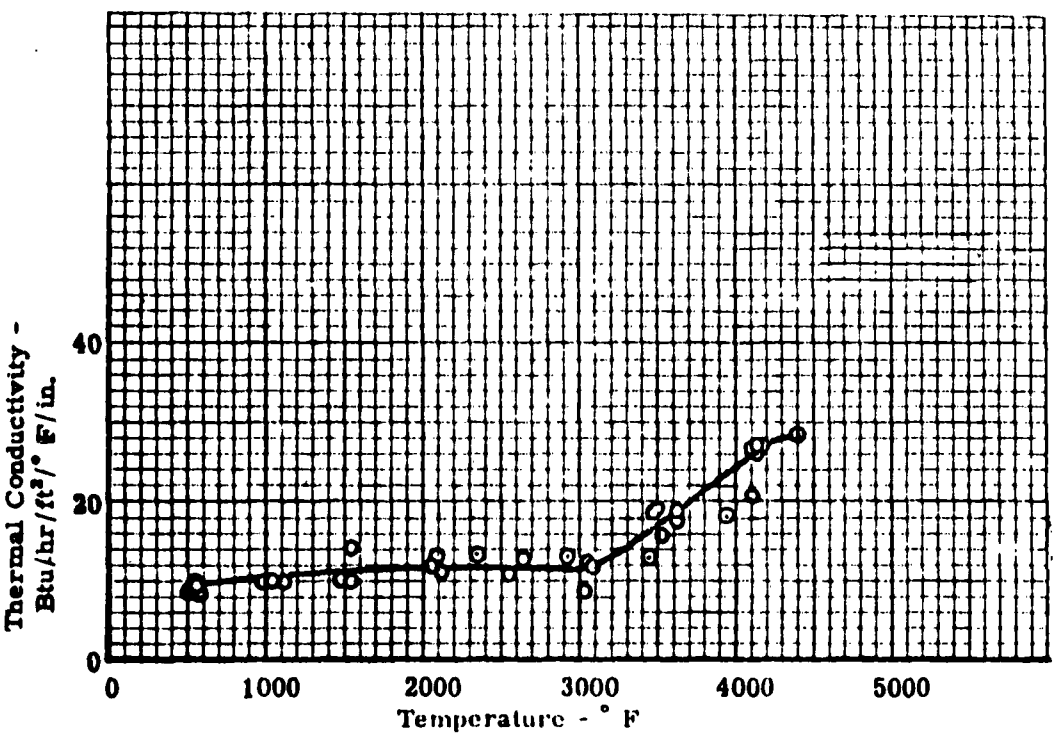


Figure 11 Thermal Conductivity of Stabilized Zirconia, 2.17% CaO, Coarse Extruded

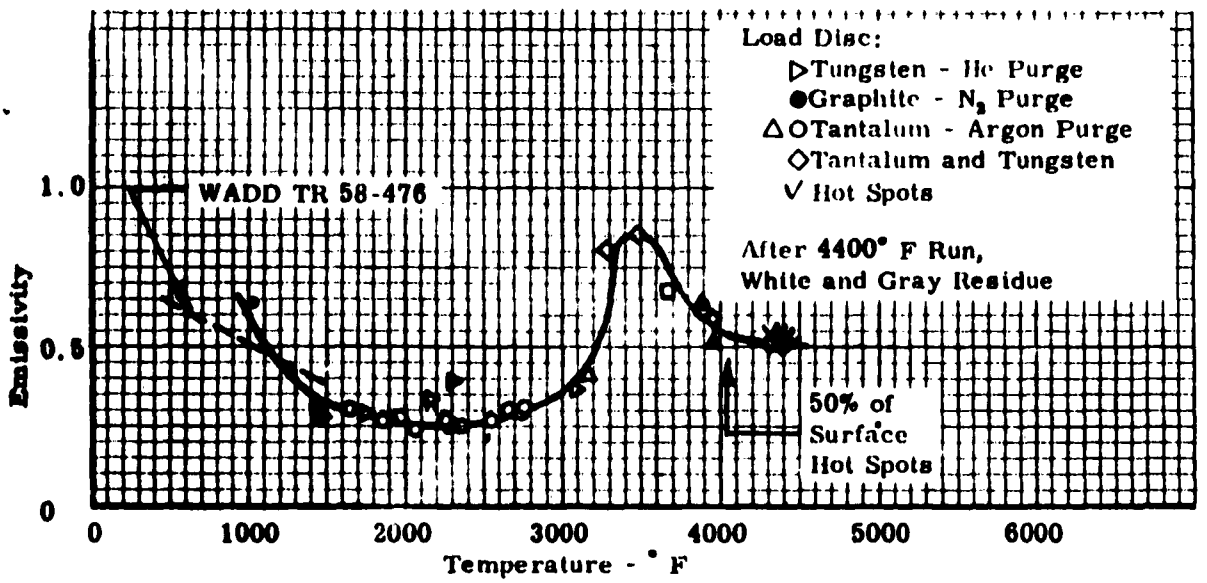


Figure 12 Total Normal Emittance of Zirconia, 2.17% CaO, Coarse.

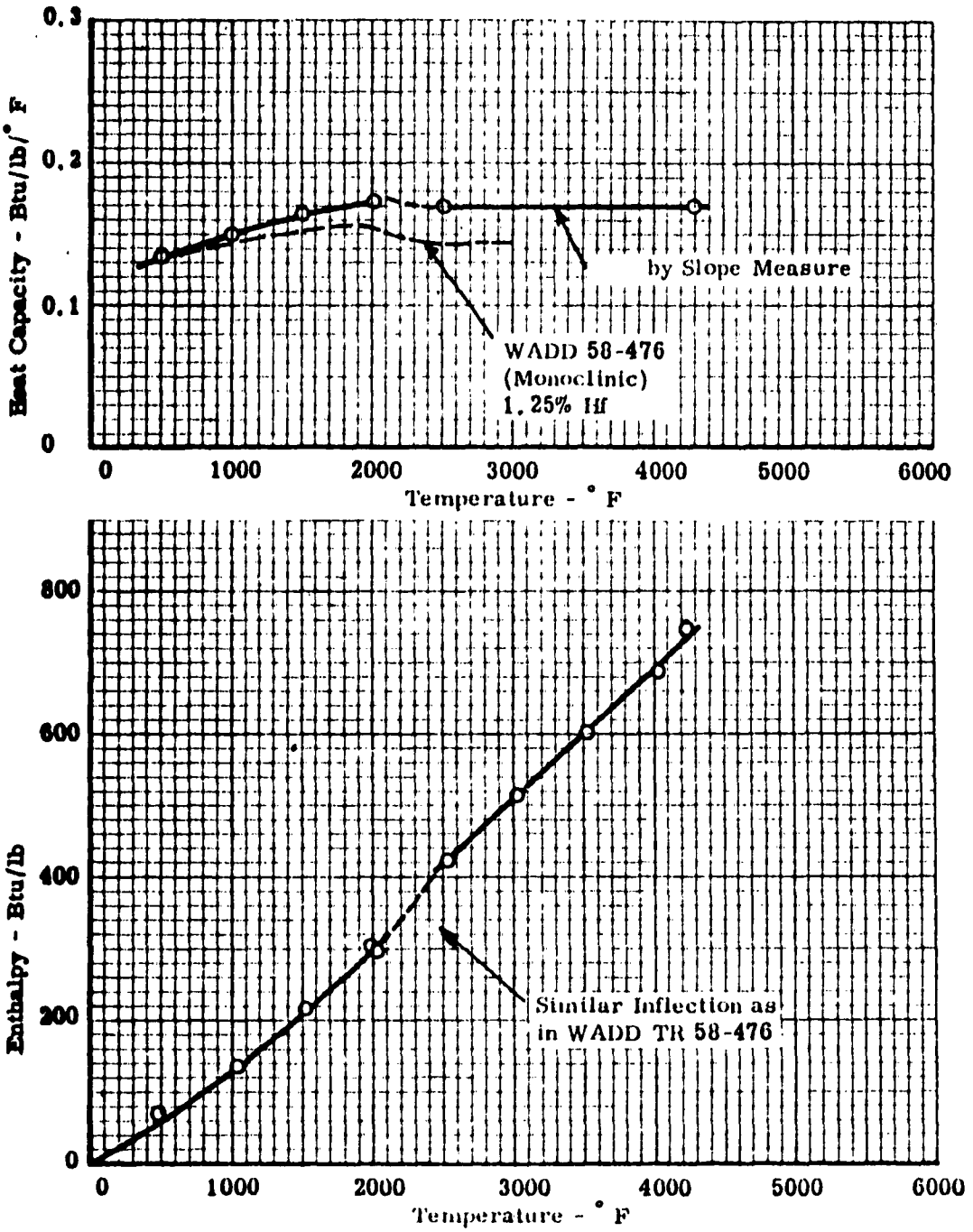


Figure 13 Enthalpy and Heat Capacity of Zirconia, 2.17 % CaO, Coarse Texture, Extruded.

Table 8

Thermal Expansion of Zirconia, 2.17% CaO, Coarse Grain, Extruded

Temperature ° F	Observed Total Elongation 10^{-3} inches	Observed Unit Elongation 10^{-3} inches/inch	Unit Elongation Correction for Dilatometer Motion 10^{-3} inches/inch	Corrected Specimen Unit Elongation 10^{-3} inches/inch
76	0	0	0	0
480	4.1	1.4	0.2	1.6
974	9.9	3.5	0.6	4.1
1490	14.7	5.1	1.2	6.3
1925	19.4	6.8	1.6	8.4
2470	26.9	9.4	2.4	11.8
3050	33.3	11.6	3.2	14.8
3510	37.4	13.0	4.0	17.0
4000	39.7	13.8	4.8	18.6
4025	39.1	13.6	4.8	18.4
4140	40.0	13.9	5.0	18.9
4310	35.0	12.2	5.3	17.5
4050	29.3	10.2	4.8	15.0
3540	19.5	6.8	4.0	10.8
3060	10.7	3.7	3.2	6.9
2500	0	0	2.4	2.4
1950	- 7.8	- 2.7	1.6	- 1.1
1580	-13.3	- 4.6	1.3	- 3.3
1282	-17.1	- 6.0	0.9	- 5.1
1000	-20.7	- 7.2	0.7	- 6.5
504	-26.9	- 9.4	0.3	- 9.1
106	-32.1	-11.2	0.1	-11.1

Initial Specimen Length = 2.871"
Final Specimen Length = 2.850"

Table 9

Thermal Conductivity of Stabilized Zirconia, 2.17% CaO
Coarse Grain, Extruded

Spec. Outer Face Temp. ° F	ΔT Across Test Section ° F	Radial Heat Flow Through ¼" Calorimeter Section, $\frac{BTU}{Hr.}$	Mean Temp. of Test Section, ° F	Thermal Conductivity of Test Section BTU/Hr/Ft²/°F/Inch
-	176	35.0	532	9.12
-	186	35.4	545	8.73
-	189	39.7	552	9.62
-	190	44.7	553	10.77
-	425	90.7	1070	9.78
-	425	90.0	1074	9.72
-	424	91.8	1076	9.92
-	441	136.4	1506	14.2
-	440	97.4	1506	10.12
-	440	92.5	1508	9.64
2420	470	125.0	2036	12.2
2430	450	136.0	2070	13.8
2410	480	116.8	2027	11.15
3110	565	163.0	2658	13.23
2990	570	132.7	2534	10.68
3540	640	174.6	3028	12.5
3520	620	159.0	3024	11.73
3450	530	108.3	3024	9.39
4030	620	220.0	3534	16.3
4030	570	234.0	3474	18.75
4020	520	217.0	3604	19.13
4030	515	197.0	3618	17.5
4480	500	291.5	4082	26.7
4490	480	278.0	4106	26.7
4490	490	290 0	4098	27.1
4480	510	222.0	4072	19.9

Table 10

Temperature Data for Zirconia, 2.17% CaO, Coarse Grain, Extruded

Thermocouple Temperature °F	Observed Optical Temperature °F	Optical Temperature Corrected for Emissivity °F	Elapse of Time from Start of Run Hrs Mins	Radiometer Output Millivolts
	3200	3260		2.3
	3420	3480		3.1
	3730	3950		3.5
	3800	3830		4.90
	4050	4400		4.45
	3890	4020		4.70
	4000	4310		4.20
	4020	4360		4.40
	4080	4340		5.00
	4060	4290		5.30
	4100	4330		5.90
	4150	4320	0-17	5.80
	3510	3670		3.00
	3660	3900		3.16
	2910	3170	0-05	1.080
	3670	3870		3.466
	3660	3940		3.089
	1500	1610	0-03	0.081
	1700	1840	0-10	0.116
	1930	2140	0-12	0.173
	2000	2220	0-16	0.204
	2190	2420	0-19	0.258
	2300	2590	0-23	0.341
	2410	2730	0-26	0.399
	2350	2660	0-28	0.347
	2600	2950	0-32	0.542
	2750	3100	0-34	0.715
	2790	3110	0-38	0.835
	2790	3110	0-40	0.835
	2800	3140	0-42	0.795

Table 10 (Continued)

Temperature Data for Zirconia, 2.17% CaO, Coarse Grain, Extruded

Thermocouple Temperature °F	Observed Optical Temperature °F	Optical Temperature Corrected for Emissivity °F	Elapse of Time from Start of Run Hrs Mins	Radiometer Output Millivolts
	1650	1740		0.097
	1430	1550	0-07	0.063
	1990	2160		0.234
	2130	2280	0-10	0.334
	2800	3080	0-15	0.884
	2930	3190	0-23	1.157
575			0-01	0.020
678			0-03	0.020
750			0-12	0.024
764			0-15	0.023
967			0-21	0.041

Table 11

Enthalpy and Heat Capacity Data for
Zirconia, 2.17% CaO, Coarse Grain, Extruded

Drop Temperature (°F)	Initial Weight (grams)	Final Weight (grams)	Enthalpy from Drop Temperature to 32°F $\left(\frac{BTU}{lb}\right)$	Heat Capacity by Slope Measurement (BTU/lb-°F)
499	22.408	22.408	64.1	0.134
1507	22.408	22.408	218.5	0.164
2015	22.408	22.418	294.0	0.173
2525	20.760	20.760	423.0	0.170
3020	20.775	20.775	517.0	0.170
3515	11.667	11.667	602.0	0.170
4015	11.552	11.552	689.0	0.170
1970	12.610	12.610	299.0	0.173
1023	12.600	12.600	137.0	0.151
4240	12.465	12.465	751.0	0.170

Y520 1.43% Lime Stabilized Zirconia, Coarse Grain, Molded
(approximately 3 mole percent lime)

This formulation consists of 30% fines and 70% grog with the following chemical composition:

	Fines	Grog
ZrO_2	99.00	97.60
CaO	0.52	1.82
SiO_2	0.28	0.12
MgO	0.28	--
$CaSO_4$	0.07	0.27
SO_4	0.05	0.17

Thermal shock tests on this material show that it will withstand 1310°F/sec (Figure 31) and is superior to all the others. This formulation is heterogenous, only partially stabilized, and thus has only moderately high thermal expansion (see Figure 14). Most of the other formulations considered in this report are completely stabilized, or very near so, and have a high, rather uniform thermal expansion (Figures 1, 2, 4, 7, 10, 15, 21, 22, and 24). The expansion for this formulation is not uniform since the monoclinic crystal contracts to form the tetragonal crystal at temperatures around 1900°F and above. The crystal inversion is detrimental to the thermal shock resistance during the inversion. The thermal shock resistance of higher temperatures is increased due to the inversion, however, because of a lower thermal expansion. Thermal shock resistance factors may be determined for this formulation only up to the point of the inversion and even these calculations are questionable due to the formulation being heterogenous. The results of the thermal shock resistance factors apply only to homogenous isotropic bodies whose physical properties are very nearly independent of temperature (Kingery Reference 2).

Temp °F	S_f	E	R
RT	9250*	4.3*	671
1000	7000*	3.8*	558
1500	6600*	2.9*	798
2000	5300*	1.5*	1360
2500	1200*	1.2*	undefined
3000	400*	0.3*	undefined
3500	400*	0.3*	undefined
4000	400*	0.3*	undefined

Geller and Yavorsky (Reference 3) show by petrographic data that the reversion of crystal form upon cooling in an unstabilized zirconia is not necessarily complete, but does tend to close the hysteresis curve. Inspection of Figure 14 shows this reversion below 1000°F. Inspection of several expansion curves show a mild tendency of some formulations to close the hysteresis curve below 1000°F.

Density = 0.168 lb/in^3

Porosity = 18.08%

Melting Point Data - Table 25

Crystal Structure Data - Table 26

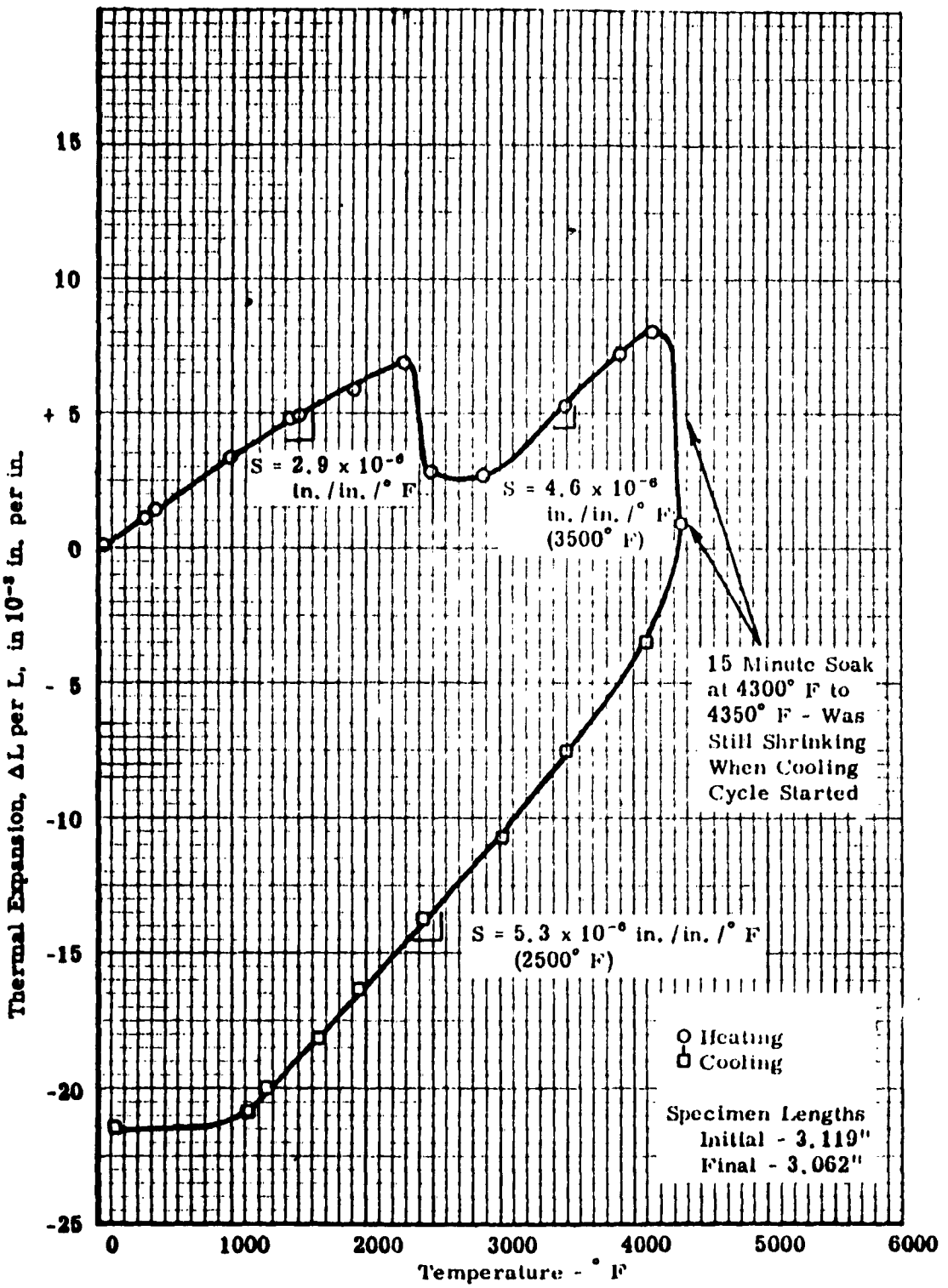


Figure 14 Thermal Expansion of Stabilized Zirconia, 1.43% CaO, Coarse Grain, Molded.

Table 12

Thermal Expansion of Stabilized Zirconia, 1.43% CaO, Coarse Grain, Molded

Temperature °F	Observed Total Elongation 10^{-3} inches	Observed Unit Elongation 10^{-3} inches/inch	Unit Elongation Correction for Dilatometer Motion 10^{-3} inches/inch	Corrected Specimen Unit Elongation 10^{-3} inches/inch
77	0	0	0	0
370	2.6	0.8	0.2	1.0
425	3.3	1.1	0.2	1.3
1000	8.5	2.7	0.6	3.3
1478	11.1	3.5	1.2	4.7
1515	11.3	3.6	1.2	4.8
1950	12.7	4.1	1.7	5.8
2300	14.3	4.6	2.2	6.8
2500	0.6	0.2	2.5	2.7
2900	- 1.2	- 0.4	3.0	2.6
3500	3.3	1.1	4.0	5.1
3925	7.8	2.5	4.6	7.1
4175	8.6	2.8	5.1	7.9
4375	-14.5	- 4.6	5.4	0.8
4100	-26.8	- 8.6	5.0	- 3.6
3500	-36.1	-11.6	4.0	- 7.6
3020	-43.7	-14.0	3.2	-10.8
2450	-50.4	-16.2	2.4	-13.8
1975	-56.5	-18.1	1.7	-16.4
1650	-60.9	-19.5	1.3	-18.2
1250	-65.5	-20.9	0.9	-20.0
1105	-67.3	-21.6	0.7	-20.9
104	-67.1	-21.5	0	-21.5

Initial Specimen Length = 3.119"
Final Specimen Length = 3.062"

Y541 2.90% Lime and 2.66% Ceria Stabilized Zirconia, Coarse Grain, Molded

This formulation consists of 30% fines and 70% grog from the same composition. The chemical analysis of this composition is as follows:

	ZrO_2	96.00			
97.1% of	CaO	2.99	and 2.9% of	CeO_2	92.0
	SiO_2	0.34		minor	
	MgO	0.21		oxides	7.6
	CaSO	0.26			
	SO_4	0.18			

Thermal shock tests on this material show that it will withstand a maximum of 79°F/sec (Figure 31) over the 2000° to 3000° range. This is not as high as would be expected by examination of the thermal shock resistance factor.

Temp °F	S_f	E	R
RT	3100*	2.6*	276
1000	2600*	2.3*	240
1500	2200*	1.9	230
2000	1600*	1.4*	210
2500	400*	0.3*	284
3000	400*	0.3*	300
3500	400*	0.3*	256
4000	400*	0.3*	undefined

Density = 0.150 lb/in^3

Porosity = 31.0%

Melting Point Data - Table 25

Crystal Structure Data - Table 26

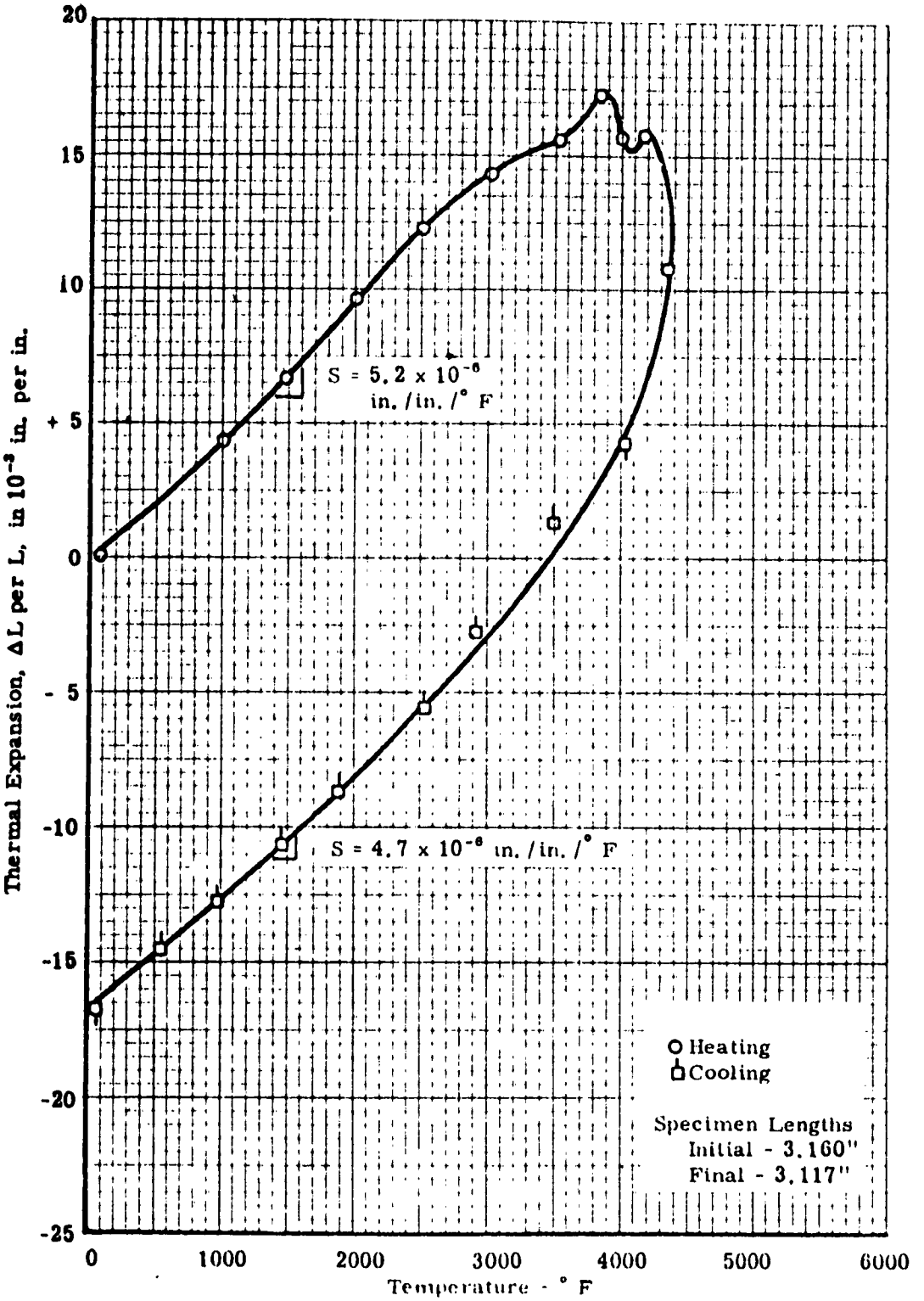


Figure 15 Thermal Expansion of Zirconia, 2.90 % CaO + 2.66 % CeO, Coarse Texture, Molded.

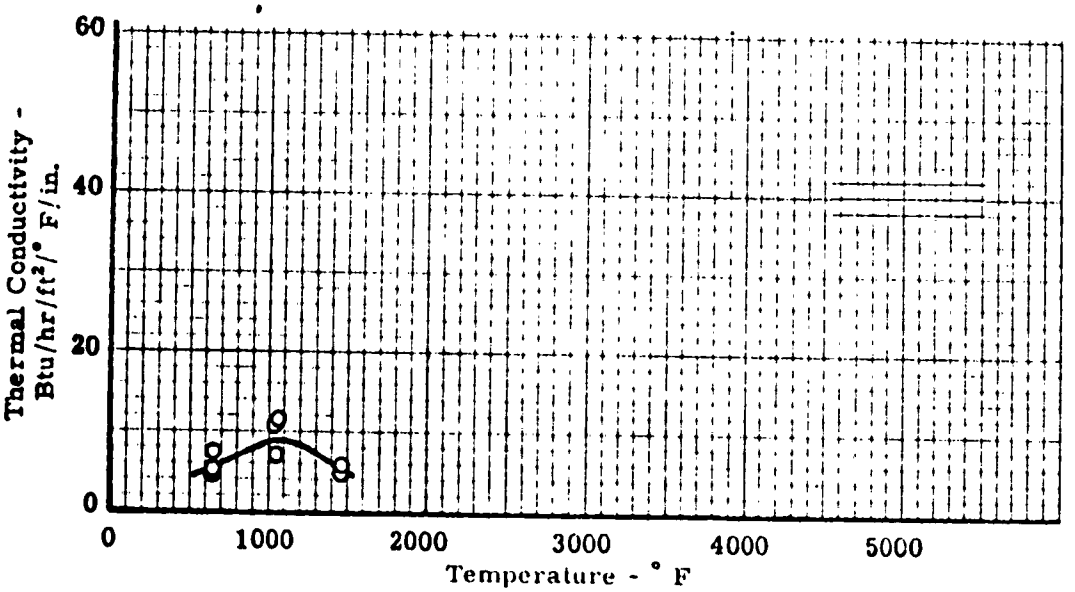


Figure 16 Thermal Conductivity of Zirconia, 2.90% CaO + 2.66% CeO_2, Coarse Molded.

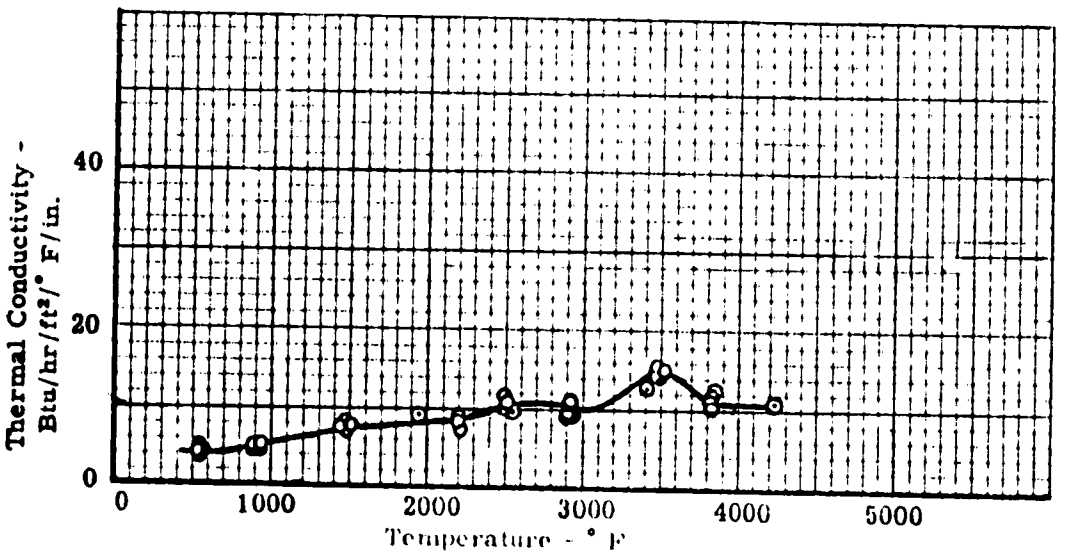


Figure 17 Thermal Conductivity of Zirconia, 2.90% CaO + 2.66% CeO_2, Coarse Molded.

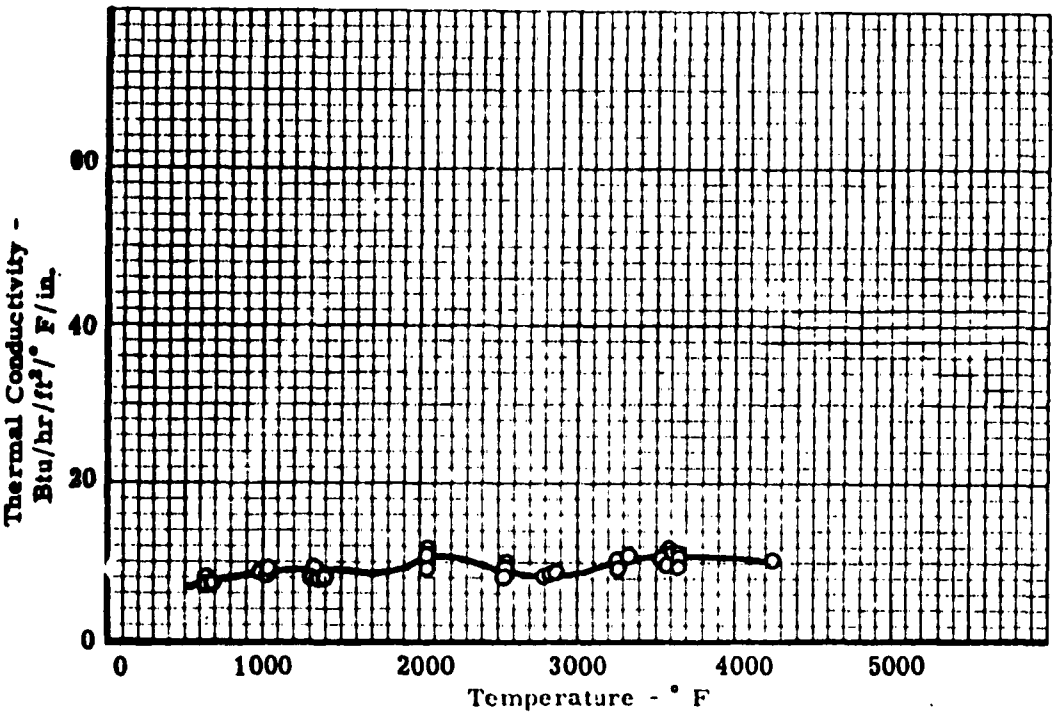


Figure 18 Thermal Conductivity of Zirconia, 2.90% CaO + 2.66% CeO_2, Coarse Molded.

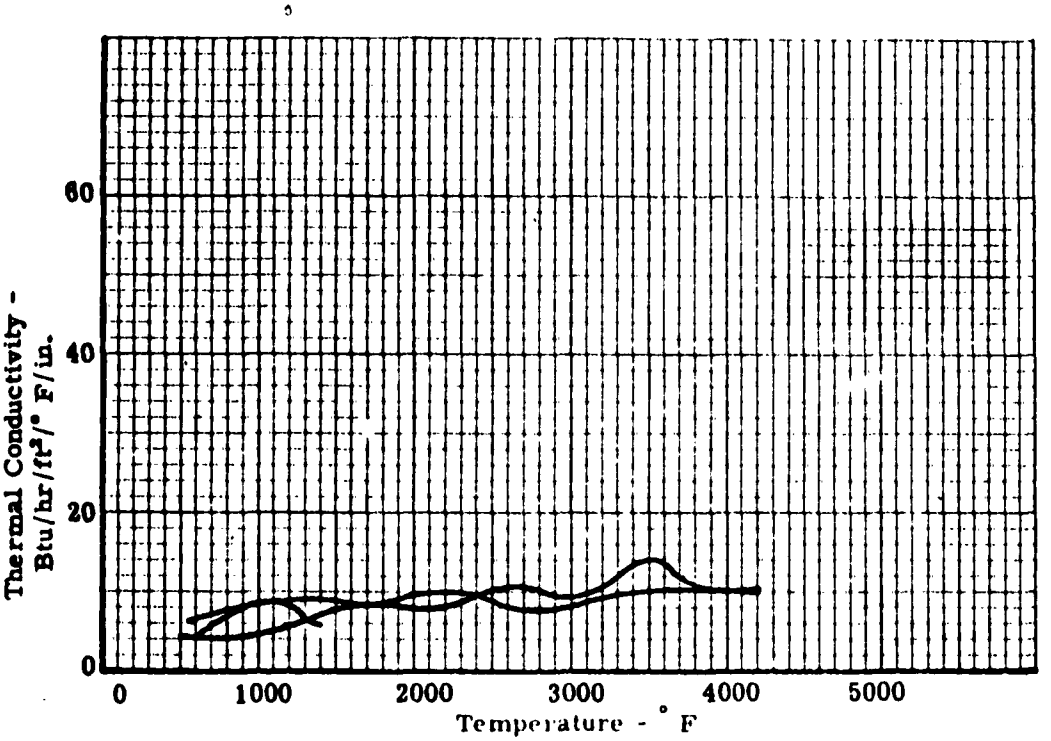


Figure 19 Thermal Conductivity of Zirconia, 2.90% CaO + 2.66% CeO_2, Coarse Molded.

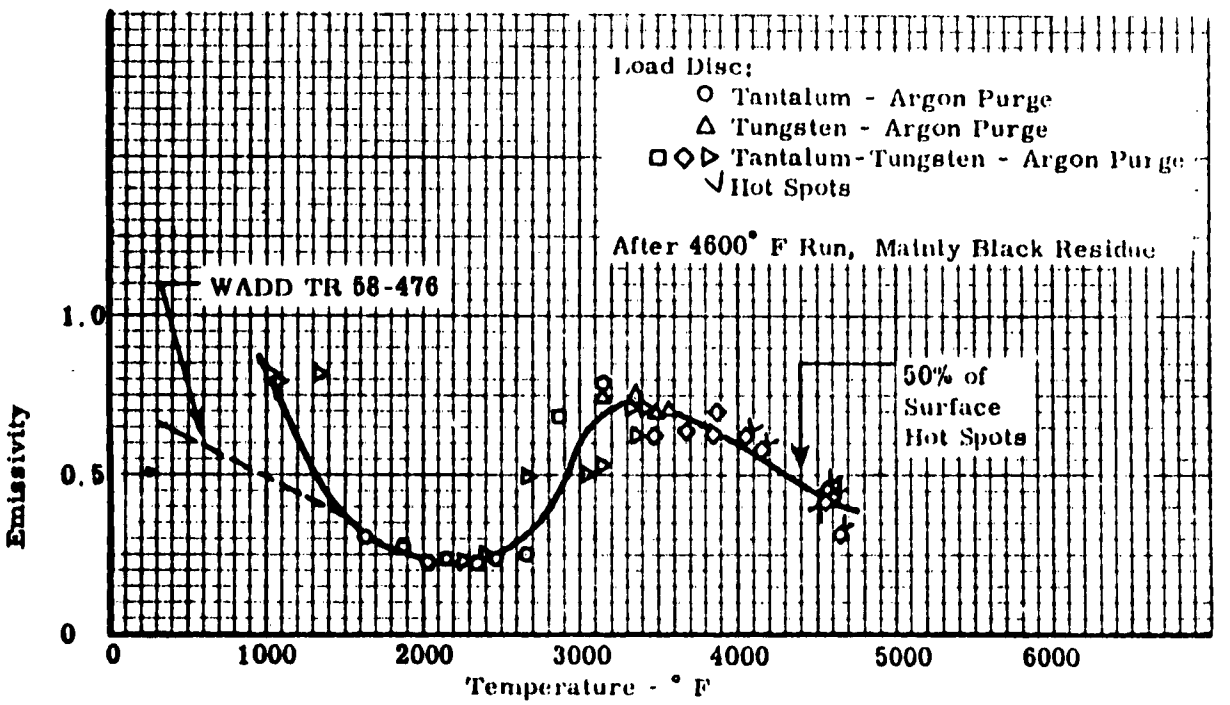


Figure 20 Total Normal Emittance of Zirconia, 2.90% CaO + 2.66% CeO_2 Coarse Molded.

Table 13

Thermal Expansion of Zirconia, 2.90% CaO + 2.66% CeO_2, Coarse Grain, Molded

Temperature °F	Observed Total Elongation 10^{-3} inches	Observed Unit Elongation 10^{-3} inches/inch	Unit Elongation Correction for Dilatometer Motion 10^{-3} inches/inch	Corrected Specimen Unit Elongation 10^{-3} inches/inch
74	0	0	0	0
1010	10.9	3.5	0.8	4.3
1498	17.2	5.4	1.2	6.6
2000	24.6	7.8	1.8	9.6
2520	31.2	9.8	2.5	12.3
3025	35.9	11.3	3.1	14.4
3450	37.5	11.8	3.8	15.6
3850	41.3	13.1	4.3	17.4
4000	34.6	10.9	4.7	15.6
4100	32.7	10.4	4.9	15.3
4175	34.3	10.8	5.0	15.8
4350	17.1	5.4	5.3	10.7
4010	2.1	- 0.65	4.8	4.1
3525	- 8.6	- 2.7	4.0	1.3
2950	-18.0	- 5.7	3.0	- 2.7
2460	-24.9	- 7.9	2.3	- 5.6
1900	-32.6	-10.3	1.6	- 8.7
1475	-36.4	-11.5	1.2	-10.3
995	-42.9	-13.6	0.7	-12.9
535	-47.3	-14.9	0.4	-14.5
70	-52.6	-16.7	0	-16.7

Initial Specimen Length = 3.160"
Final Specimen Length = 3.117"

Table 14

Thermal Conductivity of Zirconia, 2.90% CaO + 2.66% CeO_2, Coarse Grain, Molded

Spec. Outer Face Temp. °F	ΔT Across Test Section °F	Radial Heat Flow Through $\frac{1}{4}$" Calorimeter Section, $\frac{BTU}{Hr.}$	Mean Temp. of Test Section, °F	Thermal Conductivity of Test Section BTU/Hr/Ft²/°F/Inch
-	219	16.8	619	4.38
-	219	18.4	630	4.78
-	220	30.0	630	7.79
-	377	46.4	1075	7.04
-	376	76.4	1078	11.6
-	382	78.8	1098	11.8
-	532	42.1	1467	4.53
-	540	50.0	1499	5.29

Table 15

Thermal Conductivity of Zirconia, 2.90% CaO + 2.66% CeO_2, Coarse Grain, Molded

Spec. Outer Face Temp. °F	ΔT Across Test Section °F	Radial Heat Flow Through ¼" Calorimeter Section, BTU/Hr.	Mean Temp. of Test Section, °F	Thermal Conductivity of Test Section BTU/Hr/Ft²/°F/Inch
-	153	10.2	583	3.80
-	167	10.7	568	3.66
-	166	13.6	565	4.67
-	166	13.1	563	4.50
-	317	20.5	903	3.66
-	320	27.4	908	4.88
-	319	18.5	925	3.30
-	317	23.2	938	4.17
2030	557	73.6	1486	7.54
2030	556	64.0	1489	6.55
2030	551	61.7	1487	6.39
2035	553	67.9	1485	6.98
2035	556	76.1	1487	7.79
2575	470	64.9	2214	7.85
2575	470	51.0	2214	6.18
2570	475	71.5	2210	8.59
3020	660	109.0	2513	9.43
3020	660	128.0	2513	11.05
3020	660	120.0	2513	10.3
3020	600	106.0	2568	10.1
3460	710	115.0	2914	9.25
3460	710	100.0	2914	8.03
3500	710	127.0	2954	10.2
3500	710	100.0	2954	8.03
3940	590	147.0	3486	14.2
3940	590	142.0	3486	13.7
3950	570	148.0	3512	14.8
3960	590	160.0	3506	15.5
4360	680	126.0	3837	10.5
4360	680	137.0	3837	11.5
4360	680	109.0	3837	9.2

Table 16

Thermal Conductivity of Zirconia, 2.90% CaO + 2.66% CeO_2, Coarse Grain, Molded

Spec. Outer Face Temp. ° F	ΔT Across Test Section ° F	Radial Heat Flow Through $\frac{1}{4}$" Calorimeter Section, $\frac{BTU}{Hr}$	Mean Temp. of Test Section, °F	Thermal Conductivity of Test Section BTU/Hr/Ft²/°F/Inch
-	225	30 1	633	7. 64
-	226	27 5	637	6. 95
-	225	28. 8	639	7. 29
-	358	53. 5	1017	8. 53
-	361	58. 0	1025	9. 15
-	362	51. 4	1029	8 10
-	492	79. 2	1334	9. 18
-	502	66. 7	1346	7. 59
-	503	65. 6	1355	7 43
-	508	69. 8	1363	7. 84
2430	485	102 0	2058	12. 0
2430	485	96. 5	2058	11. 3
2450	520	85 1	2050	9. 3
3110	790	125. 0	2503	9. 02
3110	815	131. 0	2484	9. 17
3120	845	125. 0	2470	8. 44
3630	1055	158. 0	2816	8 54
3630	1055	150 0	2816	8. 11
3660	1060	154. 0	2843	8. 27
4020	935	169 0	3302	10. 3
4020	950	161. 0	3290	9. 65
4020	950	171 0	3290	10 3
4300	1025	176 0	3512	9 80
4300	1025	180. 0	3512	10 4
4310	1035	180. 0	3515	10. 4
4330	1075	187 0	3505	9. 91
4420	1075	211 0	3595	11 2
4460	1075	199 0	3635	10. 5
4460	1075	187. 0	3635	9. 92

Table 17

Temperature Data for Zirconia, 2.90% CaO, 2.66% CeO_2, Coarse Grain, Molded

Thermocouple Temperature °F	Observed Optical Temperature °F	Optical Temperature Corrected for Emissivity °F	Elapse of Time from Start of Run Hrs Mins	Radiometer Output Millivolts
	3310	3480		2.20
	3500	3680		2.80
	3610	3840		3.11
	3700	3870		3.61
	3810	4040		3.90
	4110	4570		4.20
	4040	4620		3.05
	4060	4550		3.90
	3900	4180		4.05
	3020	3110		1.875
	3200	3320		2.140
	3330	3490		2.350
	3370	3540		2.570
1046				0.061
1081				0.064
1358				0.124
	2100	2380		0.197
	2160	2430		0.271
	2460	2630		0.624
	2820	3040		1.063
	2950	3150		1.367
	3160	3330		1.898
	3210	3335		2.145
	1510	1635		0.078
	1710	1880		0.104
	1810	2030		0.122
	1880	2110		0.145
	2170	2455		0.238
	2350	2660		0.350
	3060	3140		1.975
	2750	2860		1.229
	2950	2990	0-06	1.880
	3540	3610	0-18	3.621

Y529 11.16 Yttria and 0.46% Lime Stabilized Zirconia, Fine Grain, Extruded (0.132% CeO_2 with the Y_2O_3)

This formulation consists of 100% fines from a composition that has the following chemical analysis:

	ZrO_2	99.00		Y_2O_3	93.00
88% of	CaO	0.52	and 12% of	CeO_2	1.10
	SiO_2	0.28			
	MgO	0.28		minor	
	$CaSO_4$	0.07		oxides	4.97
	SO_4	0.05			

There is no thermal shock data on this material. The quantitative indication of the thermal shock resistance is as follows:

Temp °F	E	S_f	R
RT	15000*	5.4*	695
1000	10600*	4.6*	452
1500	9700*	3.5*	543
2000	7300*	1.6*	1070
2500	1200*	0.4*	699
3000	400*	0.3*	334
3500	400*	0.3*	166
4000	400*	0.3*	undefined

It may be noted that these results are very similar to those obtained for 3% lime stabilized zirconia, fine grain, molded, and for 3% lime stabilized zirconia, fine grain, extruded until the higher temperatures (2500° to 3000° F) are reached.

Density = 0.176 lb/in^3

Porosity - 20.13%

Melting Point Data - Table 25

Crystal Structure Data - Table 26

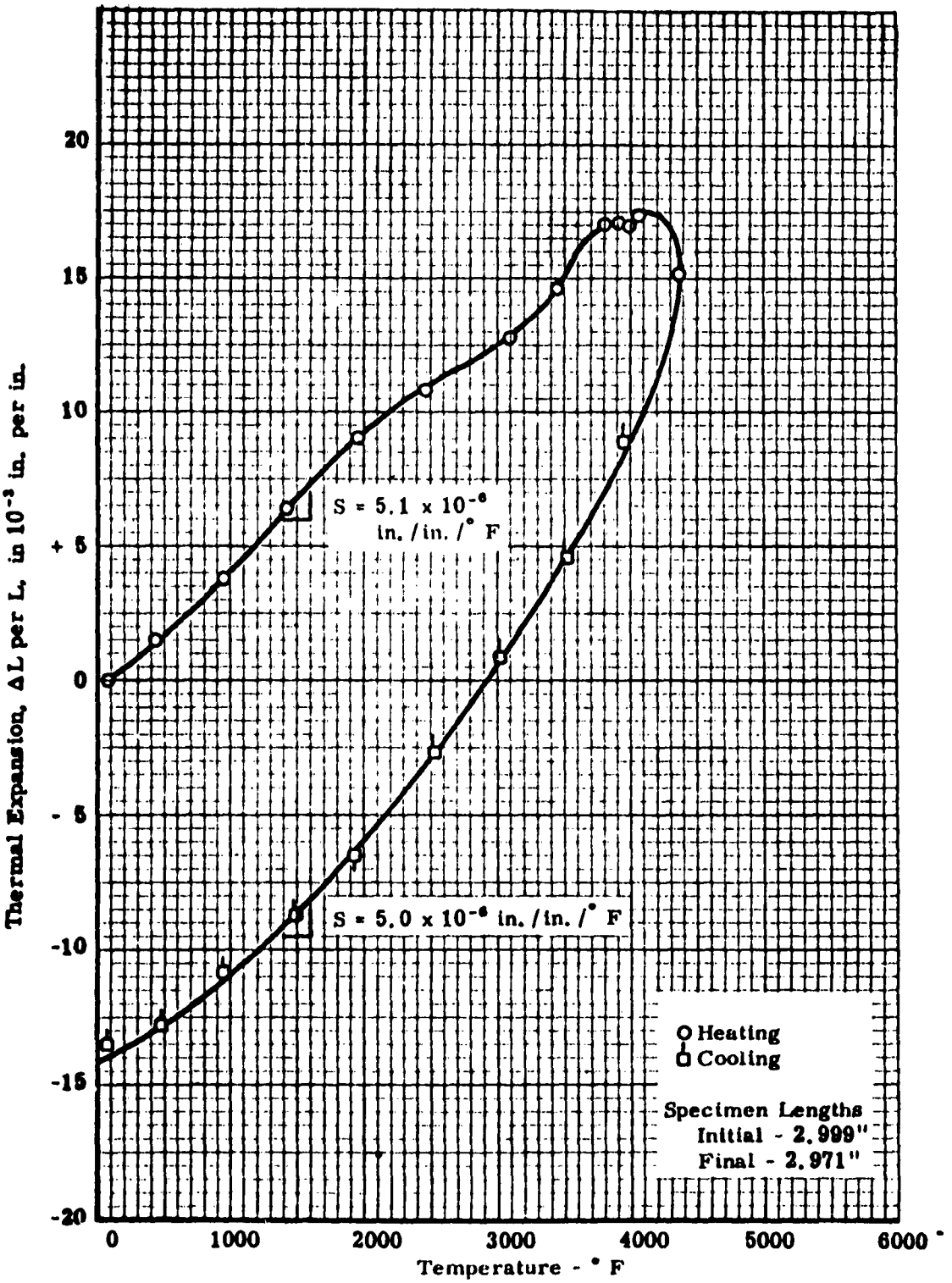


Figure 21 Thermal Expansion of Zirconia, 11.16% Y_2O_3 + .46 % CaO Fine Grain, Extruded.

Table 18

Thermal Expansion of Zirconia, 11.16% Y_2O_3, and 0.46% CaO, Fine Grain, Extruded

Temperature °F	Observed Total Elongation 10^{-3} inches	Observed Unit Elongation 10^{-3} inches/inch	Unit Elongation Correction for Dilatometer Motion 10^{-3} inches/inch	Corrected Specimen Unit Elongation 10^{-3} inches/inch
77	0	0	0	0
455	3.3	1.1	0.4	1.5
960	9.1	3.1	0.7	3.8
1435	15.6	5.2	1.2	6.4
1960	21.9	7.3	1.7	9.0
2475	25.6	8.5	2.4	10.9
3100	28.8	9.6	3.2	12.8
3450	32.8	10.9	3.8	14.7
3800	37.8	12.6	4.4	17.0
3920	37.5	12.5	4.6	17.1
4000	37.1	12.3	4.7	17.0
4050	37.9	12.6	4.8	17.4
4375	29.4	9.8	5.3	15.1
3950	12.9	4.3	4.6	8.9
3525	2.4	0.80	3.9	4.7
3030	- 6.7	- 2.2	3.1	0.9
2550	-15.4	- 5.1	2.5	- 2.6
1925	-23.9	- 8.0	1.7	- 6.3
1500	-29.8	- 9.9	1.2	- 8.7
960	-33.2	-11.1	0.8	-10.3
485	-39.5	-13.2	0.4	-12.8
345	-45.0	-15.0	0.3	-14.7
245	-46.0	-15.3	0.1	-15.2

Initial Specimen Length = 2.999"
Final Specimen Length = 2.971"

Y492 7.44% Yttria and 0.4% Lime Stabilized Zirconia Coarse Grain, Extruded (0.088% CeO_2 with the Y_2O_3)

This formulation consists of 30% fines and 70% grog from the same composition. The chemical analysis of this composition is as follows:

92% of	ZrO_2	99.00	and 8% of	Y_2O_3	93.00
	CaO	0.52		CeO_2	1.10
	SiO_2	0.28			
	MgO	0.28		minor	
	$CaSO_4$	0.07		oxides	4.97
	SO_4	0.05			

The thermal shock tests show that this material will not withstand 24°F/sec. This is not consistent with the quantitative resistance calculated.

Temp °F	S_t	E	R
RT	4250	2.8	400
1000	3000*	2.4	260
1500	2600*	1.9*	312
2000	1800*	1.4*	320
2500	400*	0.3*	370
3000	400*	0.3*	undefined
3500	400*	0.3*	undefined
4000	400*	0.3*	undefined

Density = 0.154 lb/in^3

Porosity = 27.74%

Melting Point Data - Table 25

Crystal Structure Data - Table 26

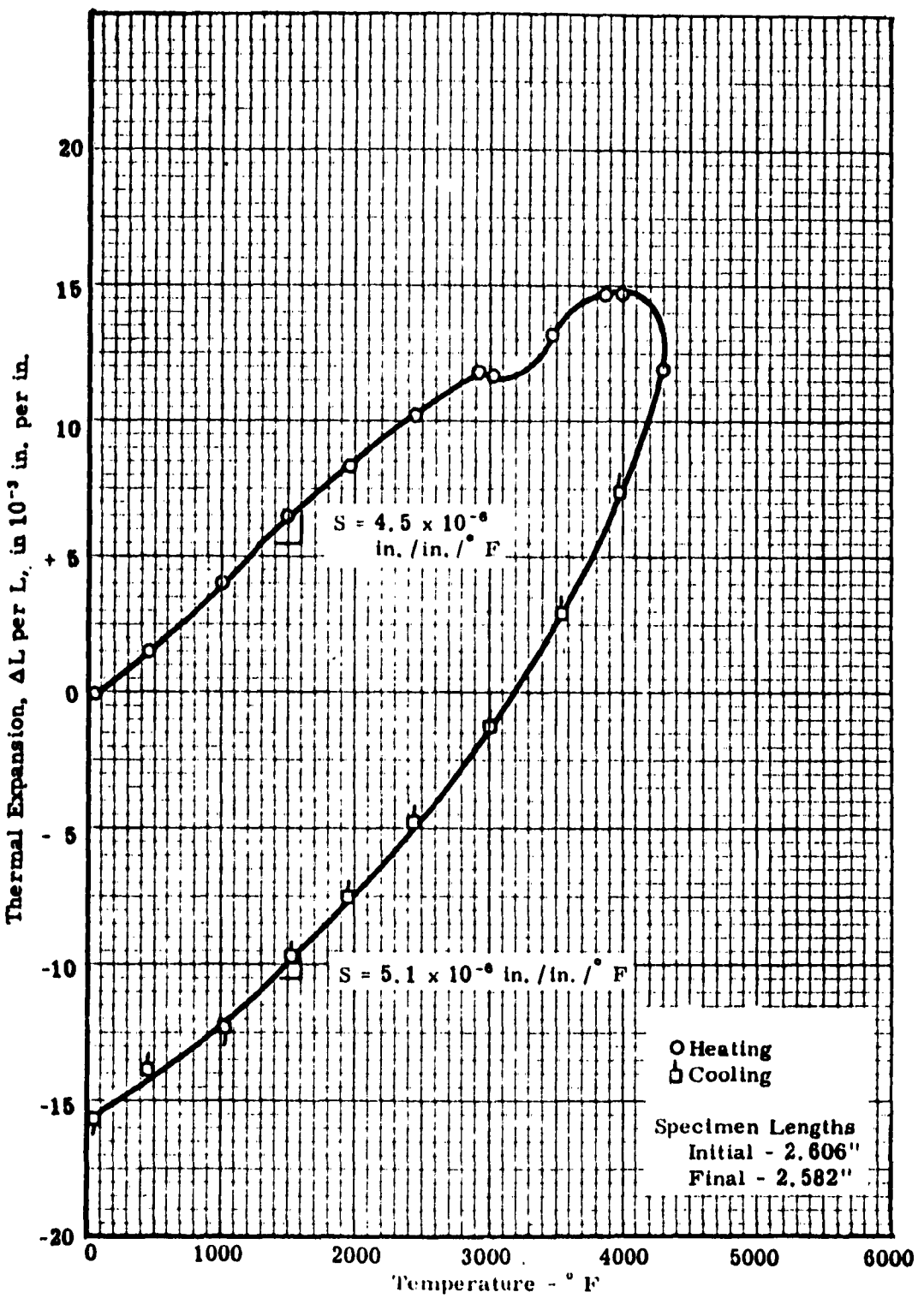


Figure 22 Thermal Expansion of Zirconia, 7.44% Y_2O_3+.47% CaO, Coarse Texture, Extruded.

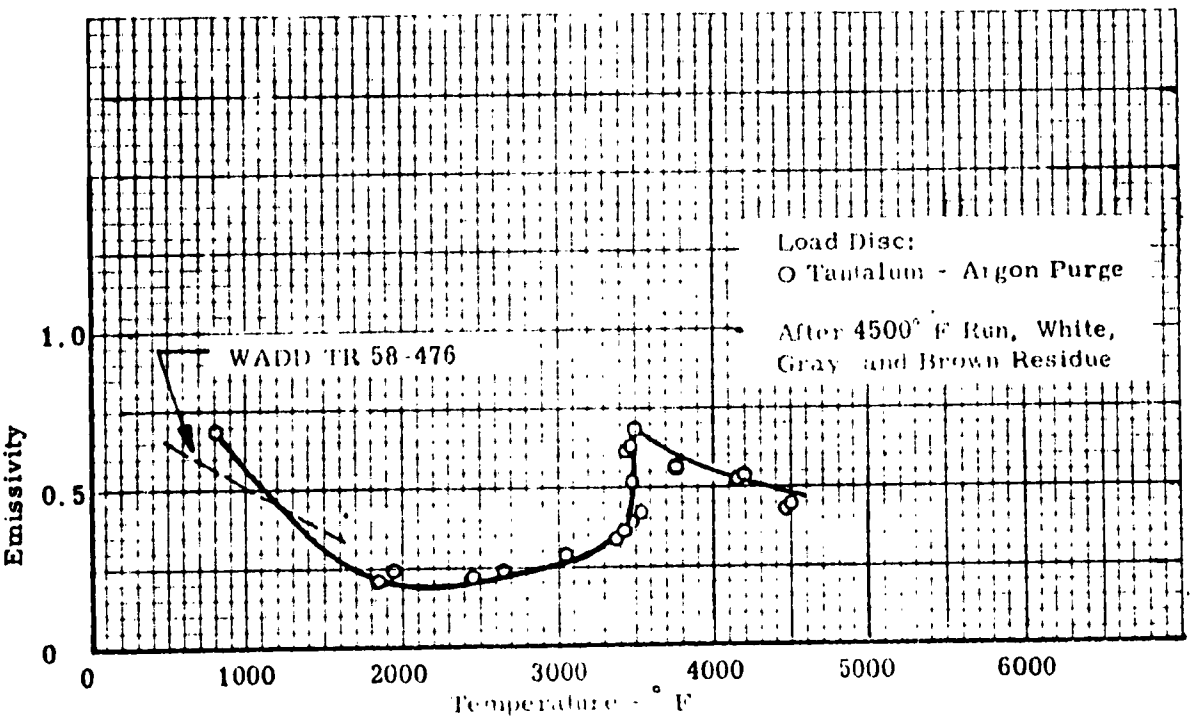


Figure 23 Total Normal Emittance of Zirconia, 7.44% Y_2O_3-7.47% CaO Coarse, Extruded.

Table 19

Thermal Expansion of Zirconia, 7.44% Y_2O_3, and 0.47% CaO, Coarse Grain, Extruded

Temperature ° F	Observed Total Elongation 10^{-3} inches	Observed Unit Elongation 10^{-3} inches/inch	Unit Elongation Correction for Dilatometer Motion 10^{-3} inches/inch	Corrected Specimen Unit Elongation 10^{-3} inches/inch
74	0	0	0	0
470	3.4	1.3	0.3	1.6
1005	8.9	3.4	0.7	4.1
1505	13.7	5.3	1.2	6.5
1990	17.4	6.7	1.7	8.4
2475	20.5	7.8	2.4	10.2
2950	22.4	8.6	3.2	11.8
3050	21.7	8.3	3.3	11.6
3500	23.5	9.0	4.0	13.0
3925	27.1	10.0	4.7	14.7
4020	25.7	9.9	4.8	14.7
4325	17.1	6.6	5.3	11.9
4000	6.8	2.6	4.7	7.3
3575	- 2.8	- 1.1	4.0	2.9
3050	-11.5	- 4.4	3.2	- 1.2
2475	-18.6	- 7.2	2.4	- 4.8
1960	-23.6	- 9.1	1.7	- 7.4
1540	-28.4	-10.9	1.3	- 9.6
1055	-34.1	-13.1	0.8	-12.3
575	-37.2	-14.3	0.5	-13.8
0	-40.7	-15.6	0	-15.6

Initial Specimen Length = 2.606"
Final Specimen Length = 2.582"

Table 20

Temperature Data for Zirconia, 7.44% Y_2O_3, and 0.47% CaO, Coarse Grain, Extruded

Thermocouple Temperature °F	Observed Optical Temperature °F	Optical Temperature Corrected for Emissivity °F	Elapse of Time from Start of Run Hrs Mins	Radiometer Output Millivolts
720				0.029
906				0.0370
	1750	1930		0.112
	1660	1830		0.080
	2170	2450		0.237
	2350	2660		0.351
	2700	3030		0.661
	2980	3340		1.034
	3020	3380		1.136
	3100	3430		1.368
	3160	3490		1.427
	3190	3500		1.583
	3200	3480		1.933
	3280	3450		2.233
	3310	3460		2.410
	3530	3760		2.68
	3860	4160		3.52
	3890	4180		3.74
	3930	4320		3.65
	4010	4450		3.73
	4050	4480		4.03
	2690	2770		1.170
	1830	1870		0.292
	1600	1640		0.185
	2650	2750		1.037
	2770	2850		1.337
	3320	3430		2.572
	3720	3870		3.785

Y538 7.09% Yttria, 2.67% Ceria, and 0.46% Lime Stabilized Zirconia, Coarse Grain, Molded

This formulation consists of 30% fines and 70% grog with the following chemical composition:

89.3% of	ZrO_2	99.00
	CaO	0.52
	SiO_2	0.28
	MgO	0.28
	$CaSO_4$	0.07
	SO_4	0.05
7.8% of	Y_2O_3	90.90
	CeO_2	0.80
	minor oxides	4.27
2.9% of	CeO_2	92.0+
	minor oxides	7.6

Thermal shock tests on this material show that it will withstand 75°F/sec (Figure 31) in the 2000°F to 3000°F range. The quantitative resistance factor shows that the failure most likely occurred when the temperature approached the 3000°F range.

Temp °F	S_f	E	R
RT	8850*	4.1*	502
1000	6600*	3.7*	364
1500	6200*	2.7*	442
2000	5000*	5.0*	667
2500	1200*	0.6*	576
3000	400*	0.3*	234
3500	400*	0.3*	230
4000	400*	0.3*	undefined

Density = 0.167 lb/in^3

Porosity = 22.58%

Melting Point Data - Table 25

Crystal Structure Data - Table 26

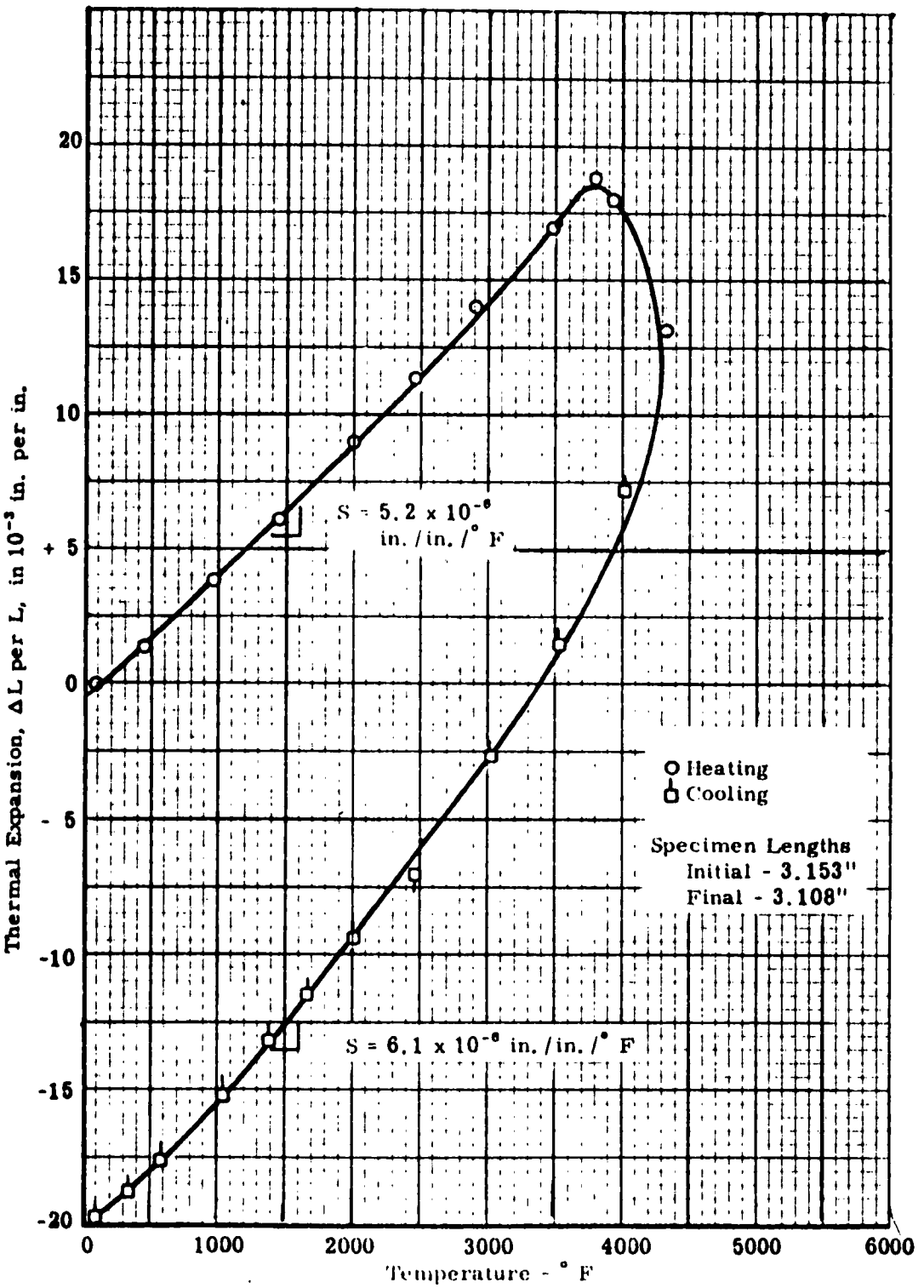


Figure 24 Thermal Expansion of Zirconia, 7.09 % Y_2O_3+2.67 % CaO+.46 % CaO Coarse Grain, Molded.

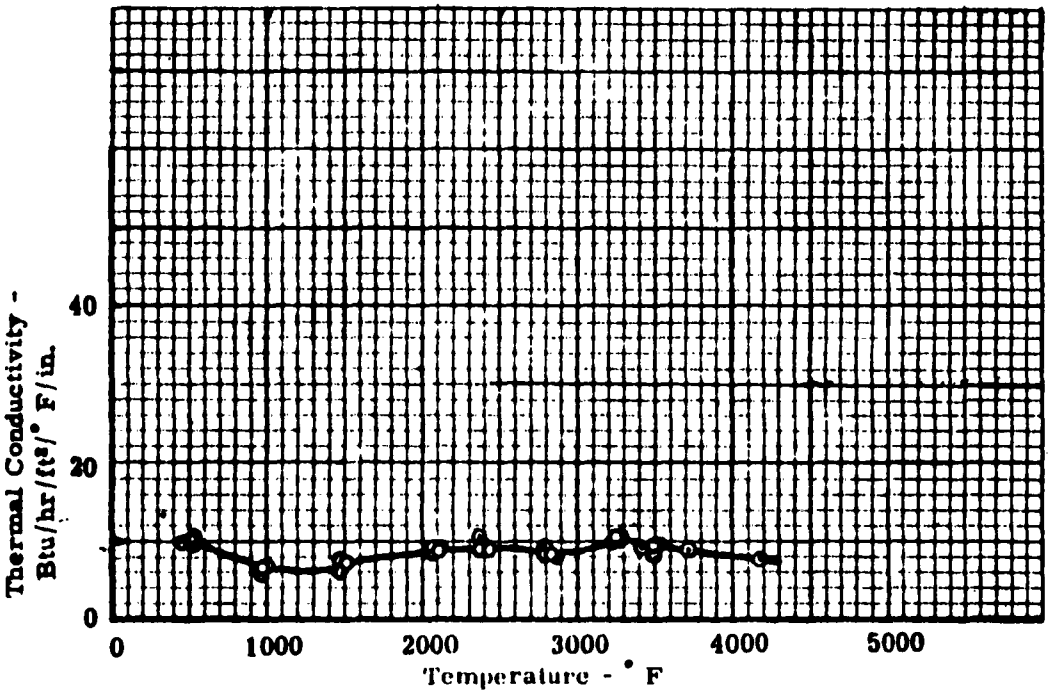


Figure 25 Thermal Conductivity of Zirconia, 7.09% Y_2O_3+2.67% CeO_2+.46% CaO Coarse Molded.

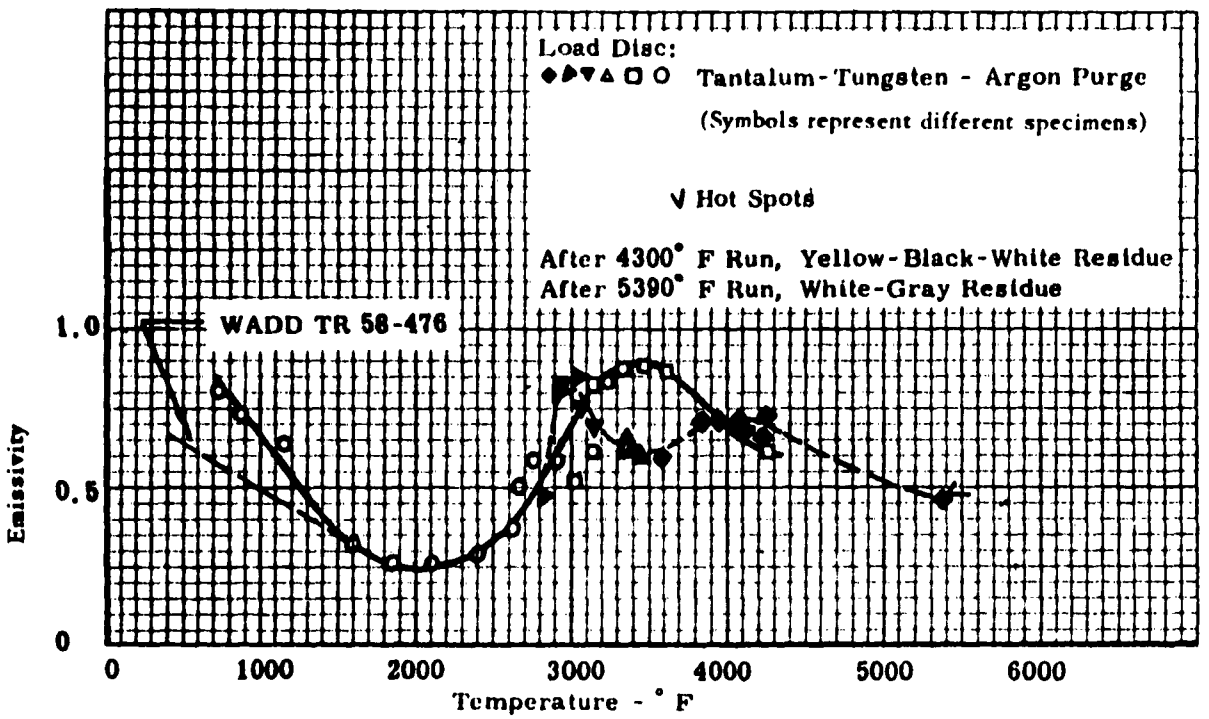


Figure 26 Total Normal Emittance of Zirconia, 7.09% Y_2O_3+2.67% Ceria +.46% CaO, Coarse Grain, Molded.

Table 21

Thermal Expansion of Zirconia, 7.09% Y_2O_3 + 2.67% CeO_2 + 0.46% CaO, Coarse Grain, Molded

Temperature ° F	Observed Total Elongation 10^{-3} inches	Observed Unit Elongation 10^{-3} inches/inch	Unit Elongation Correction for Dilatometer Motion 10^{-3} inches/inch	Corrected Specimen Unit Elongation 10^{-3} inches/inch
72	0	0	0	0
433	3.7	1.2	0.2	1.4
961	10.2	3.2	0.6	3.8
1415	16.1	5.1	1.0	6.1
1450	16.1	5.1	1.1	6.2
1975	22.9	7.3	1.7	9.0
2450	28.5	9.0	2.4	11.4
2900	34.7	11.0	3.0	14.0
3475	41.4	13.1	3.9	17.0
3800	45.5	14.4	4.5	18.9
3925	42.2	13.4	4.6	18.0
4325	25.0	7.9	5.3	13.2
4010	7.7	2.4	4.8	7.2
3540	- 8.0	- 2.5	4.0	1.5
3025	-18.2	- 5.8	3.2	- 2.6
2475	-28.5	- 9.4	2.4	- 7.0
2010	-35.4	-11.2	1.8	- 9.4
1660	-40.7	-12.9	1.4	-11.5
1385	-44.9	-14.2	1.0	-13.2
1024	-50.0	-15.9	0.7	-15.2
573	-56.6	-18.0	0.3	-17.7
320	-59.7	-19.0	0.2	-18.8
80	-62.3	-19.8	0	-19.8

Initial Specimen Length = 3.153"
Final Specimen Length = 3.108"

Table 22

Thermal Conductivity of Zirconia, 7.09% Y_2O_3 + 2.67% CeO_2 + 0.46% CaO, Coarse Grain, Molded

Spec. Outer Face Temp. °F	ΔT Across Test Section °F	Radial Heat Flow Through ¼" Calorimeter Section, BTU/Hr.	Mean Temp. of Test Section, °F	Thermal Conductivity of Test Section BTU/Hr/Ft²/°F/Inch
-	138	25.5	528	10.5
-	139	26.1	532	10.7
-	139	22.9	541	9.4
-	141	20.9	546	8.46
-	142	23.6	560	9.48
-	273	29.9	1000	6.24
-	273	26.5	1004	5.54
-	273	30.6	1006	6.39
-	399	41.2	1492	5.88
-	406	44.0	1510	6.18
-	405	46.3	1514	6.51
-	401	51.0	1517	7.22
2490	440	66.7	2152	8.65
2490	440	65.2	2152	8.45
2490	475	72 8	2125	8.75
2500	510	75.1	2108	8.39
2930	630	109.0	2446	9.88
2930	630	106.0	2446	9.60
2930	650	104.0	2430	9 12
2930	650	97.9	2430	8.58
2940	670	103 0	2425	8.77
3540	910	133.0	2840	8.34
3540	910	128.0	2840	8.01
3540	910	127 0	2840	7.95
3540	890	127.0	2855	8.14
3890	780	124.0	3290	9.05
3890	780	131.0	3290	9.56
3890	780	145.0	3290	10.6
3890	780	149.0	3290	10.9
4380	1000	159.0	3511	9.05
4380	1000	149.0	3511	8.50
4380	1000	170.0	3511	9.70

Table 23

Temperature Data for Zirconia, 7.09% Y_2O_3 + 2.67% CeO_2 + 0.46% CaO

Thermocouple Temperature °F	Observed Optical Temperature °F	Optical Temperature Corrected for Emissivity °F	Elapse of Time from Start of Run Hrs Mins	Radiometer Output Millivolts
	3390	3590		2.292
	3670	3820		3.362
	4100	4260		5.263
	3920	4080		4.441
	3800	3950		4.036
	3920	4100		4.266
	4050	4240		4.596
	4150	4240		4.626
	4840	5390	0-15	4.902
	2940	2980	0-6	1.757
	3010	3090	0-9	1.773
	3030	3140	0-11	1.751
	2930	3050	0-10	1.96
	3180	3350		2.00
	3200	3350		2.11
	3280	3470	0-12	2.115
	2750	2830	0-8	1.292
	2880	2930	0-12	1.660
	3010	3060	0-21	1.992
	2840	3030		1.145
	3000	3150		1.568
	3080	3140		2.114
	3170	3230		2.36
	3320	3370		2.836
	3420	3470		3.09
	3560	3620		3.73
	4010	4260	0-20	4.77
743				0.025
1260				0.080
1324	1490	1600	0-13	0.079
	1710	1880	0-20	0.119
	1900	2110	0-28	0.169

Table 23 (Continued)

Temperature Data for Zirconia, 7.09% Y_2O_3 + 2.67% CeO_2 + 0.46 CaO

Thermocouple Temperature °F	Observed Optical Temperature °F	Optical Temperature Corrected for Emissivity °F	Elapse of Time from Start of Run Hrs Mins	Radiometer Output Millivolts
	2160	2400	0-33	0.284
	2400	2630	0-38	0.497
	2510	2670	0-43	0.707
	2610	2750	0-48	0.943
	2750	2900	0-58	1.135

Y523 5. 20% Yttria and 0. 50% Lime Stabilized Zirconia, Coarse Grain, Molded

This formulation consists of 30% fines and 70% grog. All of the fines and 92% of the grog have the following composition:

ZrO_2	99. 00
CaO	0. 52
SiO_2	0. 28
MgO	0. 28
$CaSO_4$	0. 07
SO_4	0. 05

8% of the grog has this composition:

Y_2O_3	93. 00
CeO_2	1. 10
minor oxides	4. 97

There is no thermal shock data for this material, but when extruded it will withstand 700°F/sec up to 4000°F. The formulation is one that is only partially stabilized and is heterogenous. The inversion of the monoclinic crystal to the tetragonal occurs in tne temperature range between 1000°F and 1500°F. Thermal shock resistance factors may be determined for this formulation only up to the point of the inversion.
See page

Temp °F	S_f	E	R
RT	8200*	4. 0*	804
1000	6000*	3. 7*	549
1500	5400*	2. 6*	undefined
2000	4950*	1. 4*	undefined
2500	1200*	0. 3*	undefined
3000	400*	0. 3*	undefined
3500	400*	0. 3*	undefined
4000	400*	0. 3*	undefined

Density = 0. 165 lb/in^3

Porosity = 21. 22%

Melting Point Data - Table 85

Crystal Structure Data - Table 26

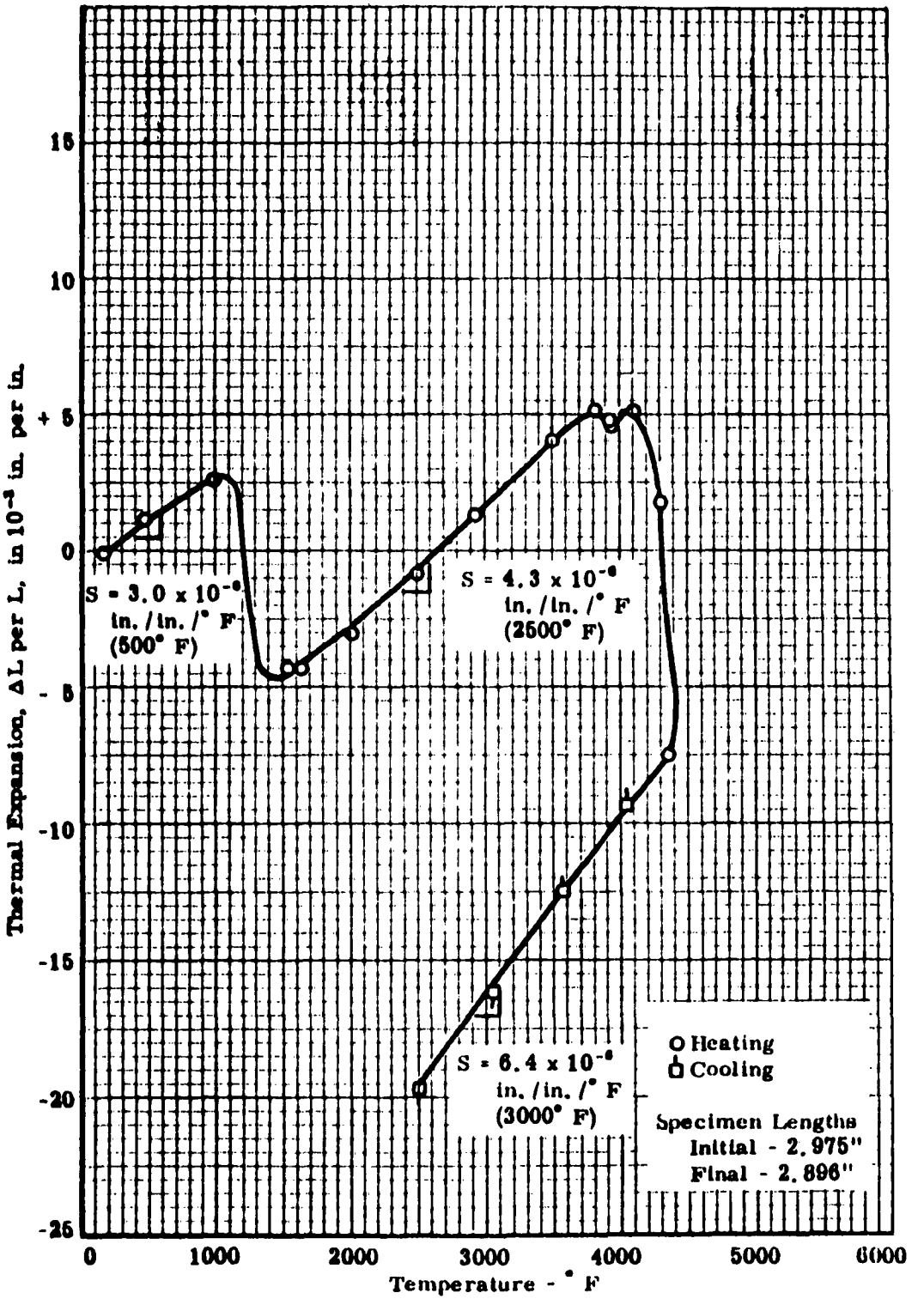


Figure 27 Thermal Expansion of Stabilized Zirconia, 5.20% Y_2O_3+.50% CaO Coarse Grain, Molded.

Table 24

Thermal Expansion of Stabilized Zirconia, 5.20% Y 0 , + 0.50% CaO, Coarse Grain, Molded

Temperature °F	Observed Total Elongation 10^{-3} inches	Observed Unit Elongation 10^{-3} inches/inch	Unit Elongation Correction for Dilatometer Motion 10^{-3} inches/inch	Corrected Specimen Unit Elongation 10^{-3} inches/inch
190	0	0	0	0
490	2.6	0.9	0.3	1.2
1004	6.0	2.0	0.7	2.7
1507	-16.2	- 5.4	1.2	- 4.2
1610	-16.3	- 5.5	1.3	- 4.2
2000	-13.9	- 4.7	1.7	- 3.0
2500	- 9.6	- 3.2	2.4	- 0.8
2910	- 5.4	- 1.8	3.1	1.3
3500	0.3	0.1	4.0	4.1
3810	2.3	0.8	4.4	5.2
3920	0.5	0.2	4.7	4.9
3950	0	0	4.7	4.7
4100	0.7	0.2	5.0	5.2
4300	-10.0	- 3.4	5.3	1.9
4350	-38.0	-12.8	5.4	- 7.4
4025	-41.8	-14.1	4.8	- 9.3
3575	-48.8	-16.4	4.1	-12.3
3050	-57.7	-19.4	3.3	-16.1
2475	-65.5	-21.9	2.4	-19.5
70	-93.8	-31.3	0	-31.3

Initial Specimen Length = 2.975"
Final Specimen Length = 2.896"

General Collected Data

For convenience, the thermal expansion curves, the thermal conductivity plots, and the emittance curves for all of the zirconia materials are combined and shown respectively in Figure 28, Figure 29, and Figure 30. Figure 31 is a bar chart showing thermal shock data.

Table 25 shows the melting point of each material, while Table 26 shows the effect of environment on the crystal structure for each material. Temperature-time history of the materials during thermal expansion are given in Table 27.

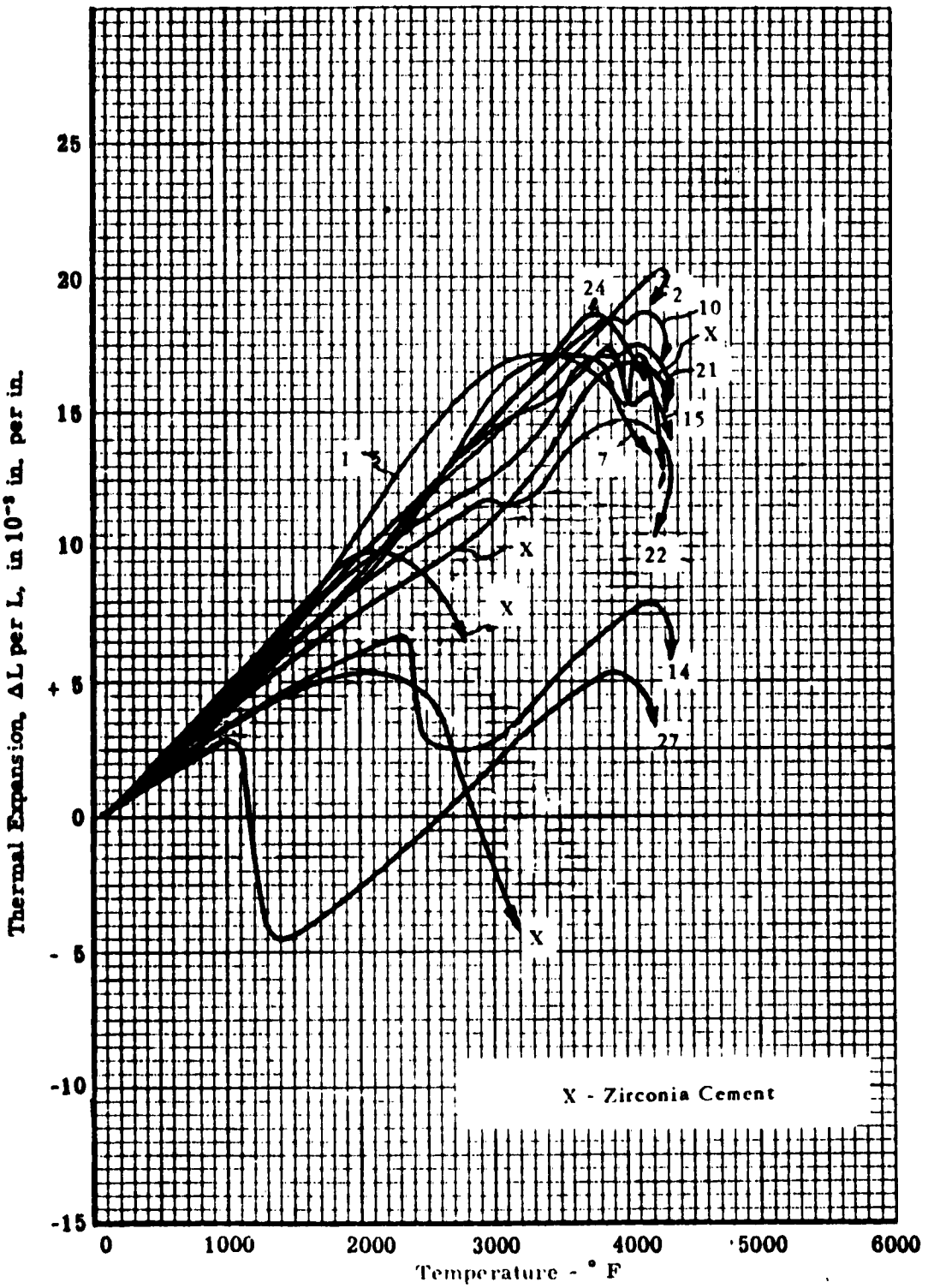


Figure 28 Composite of Thermal Expansion Curves for Zirconia Materials.

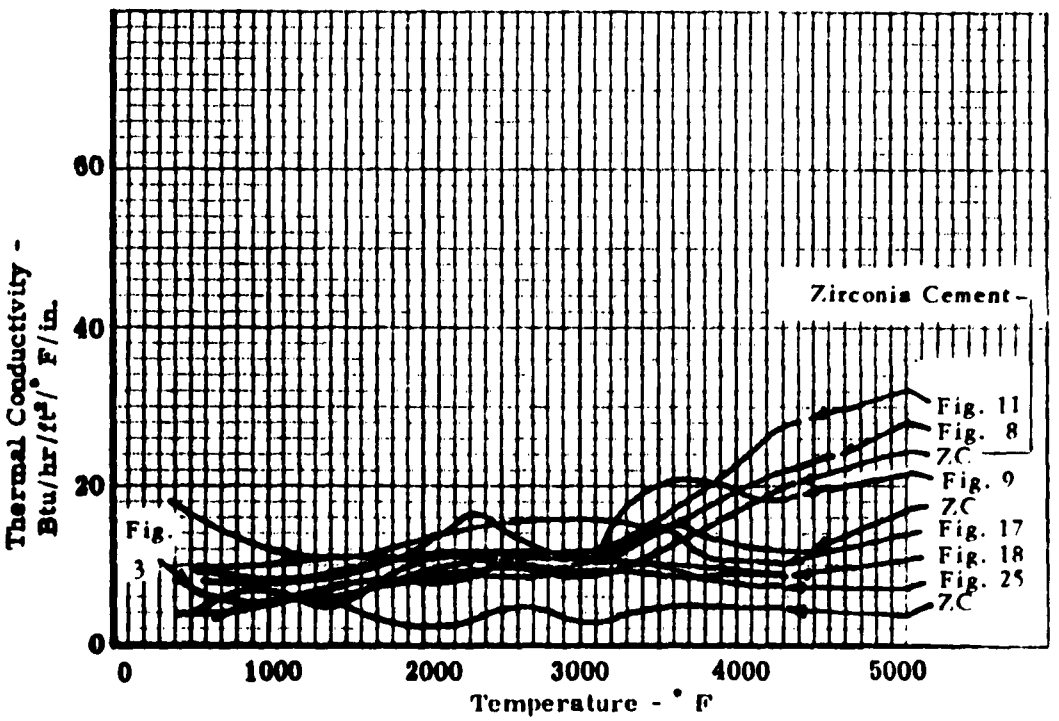


Figure 29 Composite Plot of Thermal Conductivity for Zirconia Materials.

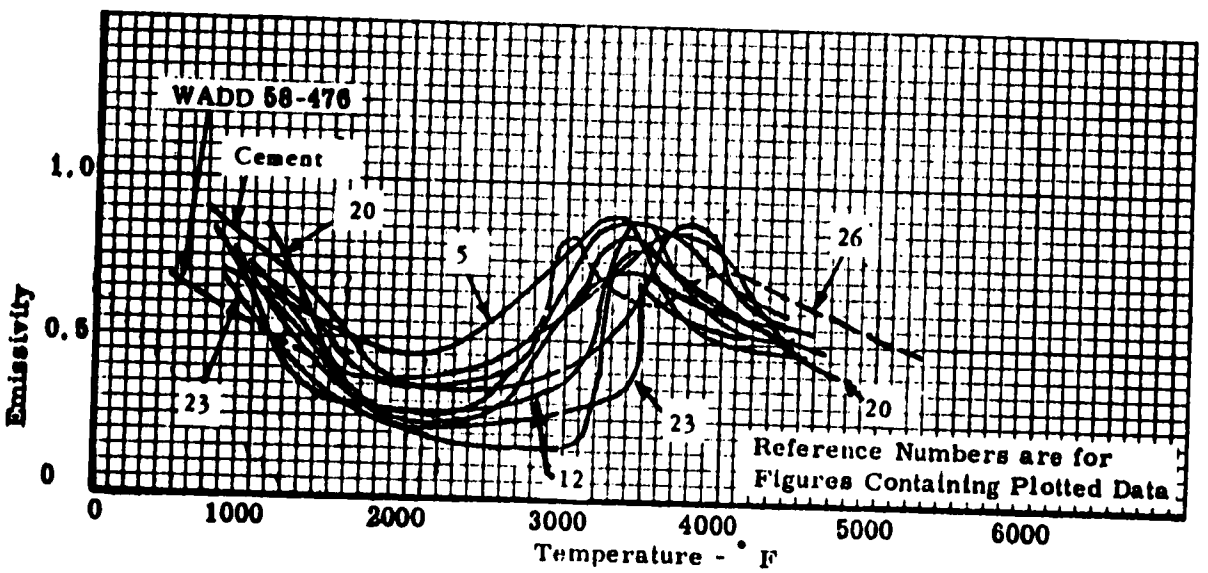


Figure 30 Composite Emittance Curves for Zirconia Formulations.

°F/SEC

10 20 40 60 80 100 200 400 600 800 1000 2000 4000 6000 8000 10000

*1/4" Rods — 3% CaO Fine Grain, Extruded

1/2" Rods — 2.17% CaO, Coarse Grain, Molded

Type I and Type II — 2.17% CaO, Coarse Grain, Molded

1/2" Rods — 2.17% CaO, Coarse Grain, Extruded

Type II — 2.17% CaO, Coarse Grain, Extruded

1/2" Rods — 2.17% CaO, Coarse Grain, Extruded With Larger Mesh Grog

Type I — 2.17% CaO, Coarse Grain, Extruded With Larger Mesh Grog

Type I — 2.17% CaO, Coarse Grain, Extruded

1/2" Rods (Heterogenous) — 1.43% CaO, Coarse Grain, Molded

*1/2" Rods — 2.90% CaO + 2.66% CeO_2, Coarse Grain, Molded

7.44% Y_2O_3 + 0.47% CaO, Coarse Grain, Extruded

*1/2" Rods — 7.09% Y_2O_3 + 2.67% CeO_2 + 0.47% CaO, Coarse Grain, Molded

1/2" Rods — 5.20% Y_2O_3 + 0.50% CaO, Coarse Grain, Extruded

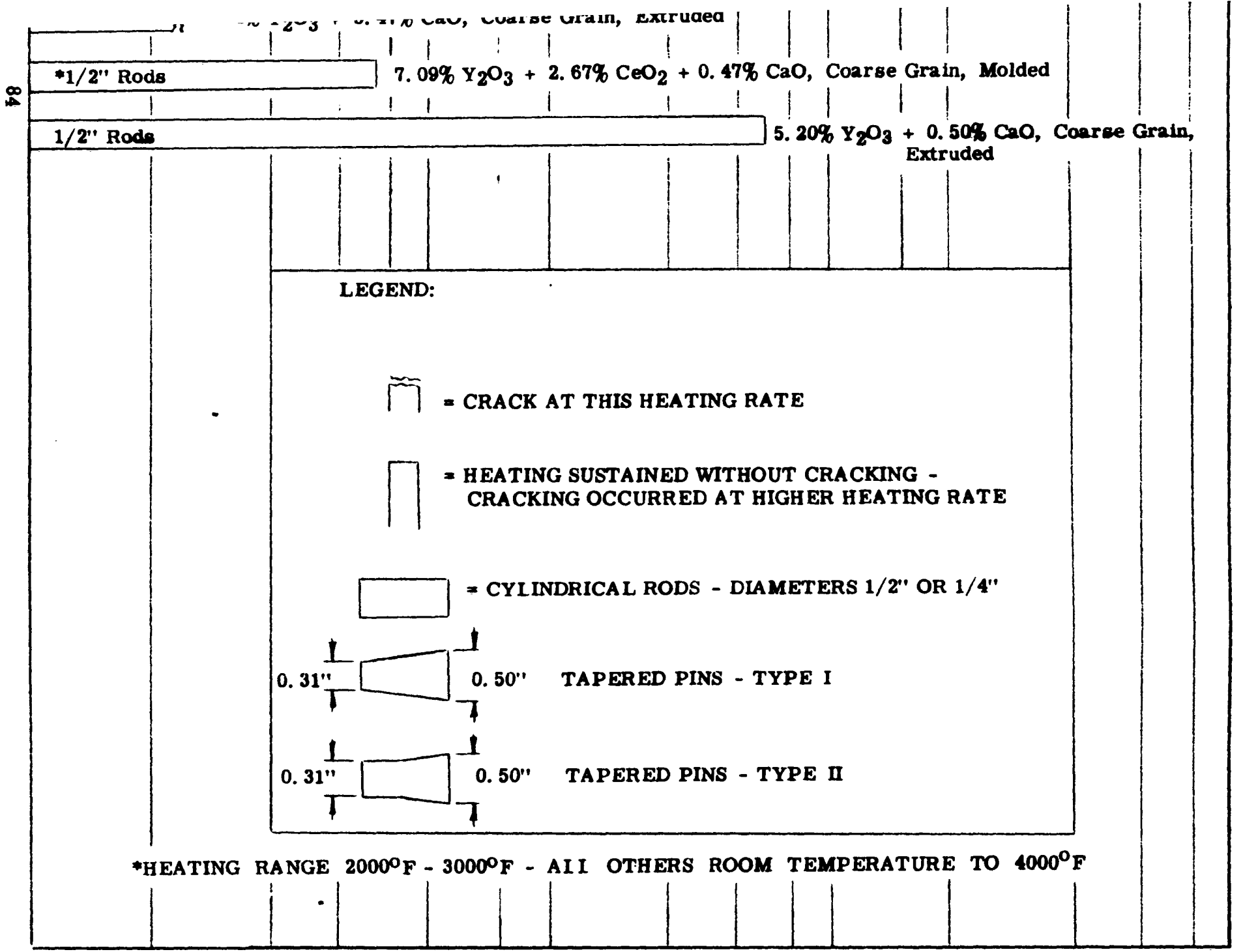


FIGURE 31 - Summary of Maximum Heating Rate Sustained By Various Grades of Sintered Zirconia

TABLE 25

MELTING POINT OF ZIRCONIA COMPOSITIONS

Description	Uncorrected Brightness Temperature at Melting - °F		
	Specimen No. 1	Specimen No. 2	Average
1.43% CaO - coarse, molded	4720	4720	4720
2.17% CaO - coarse, molded	4580	4640	4610
2.17% CaO - coarse, extruded	4660	4640	4650
3% CaO - fine, molded	4660	4680	4670
5.62% CaO - coarse, molded	4660	4640	4650
2.90% CaO / 2.66% CeO_2 - coarse, molded	4680	4680	4680
5.20% Y_2O_3 / 0.50% CaO - coarse, molded	4760	4760	4760
7.44% Y_2O_3 / 0.47% CaO - coarse, extruded	4740	4780	4760
7.09% Y_2O_3 / 2.67% CeO_2 / .46% CaO - coarse, molded	4760	4780	4770

TABLE 26

EFFECT OF ENVIRONMENT ON
ZIRCONIA CRYSTALLINE STRUCTURE

Description	% Monoclinic Before Heating	% Monoclinic After Heating
1.43% CaO - coarse, molded	44	49
2.17% CaO - coarse, molded	24	35
2.17% CaO - coarse, extruded	3-1/2	3
3% CaO - fine, extruded	7-1/2	15
2.90% CaO / 2.66% CeO_2 - coarse, molded	5	15
5.62% CaO - coarse, molded	0	0
7.44% Y_2O_3 / 0.47 CaO - coarse, extruded	2	0
7.09% Y_2O_3 / 2.67% CeO_2 / 0.46% CaO - coarse, molded	0	0

(1) Specimens were soaked 1 hour in an air atmosphere at 4000°F.

(2) X-ray diffraction patterns were run on powdered materials.

TABLE 27

Temperature-Time History of Zirconia Specimens During Runs on Thermal Expansion

Figure	Temperature °F	Time Hr.-Min.	Figure	Temperature °F	Time Hr.-Min.
1	62	0-0	15	74	0-0
	1022	0-33		1010	1-00
	1950	0-56		2000	1-28
	2960	1-23		3025	1-50
	4310	1-53		4350	2-30
	1400	2-33		1475	3-30
2	73	0-0	21	77	0
	1005	0-37		960	0-20
	1910	1-10		1960	0-45
	2970	1-38		3100	1-35
	4325	2-15		4375	2-05
	1550	3-39		1500	2-45
7	79	0-0	22	74	0-0
	1089	16-05		1005	1-13
	1975	16-43		1990	1-53
	3000	17-55		3050	2-18
	4300	19-00		4325	3-01
	1700	21-03		1540	4-06
10	76	0-0	24	0	0-0
	974	0-39		961	0-58
	1925	1-03		1975	1-37
	3050	1-29		2900	2-11
	4310	2-08		4325	2-55
	1580	3-42		1660	3-47
				80	6-00
14	77	0-0			
	1000	16-0	27	190	0-0
	1950	16-40		1004	0-23
	2900	17-13		2000	0-50
	4375	18-03		2910	1-23
	1650	18-50		4350	2-13
				2475	2-38

DISCUSSION

Phase Diagram, Zirconia-Calcia - The work reported here indicates a given amount of calcia to be more effective in stabilizing zirconia than had previously been shown by Duwez, Odell, and Brown (Reference 4), by Geller and Yavorsky (Reference 3), or by Curtis (Reference 5).

The zirconia-calcia phase diagram developed by Ruff, Ebert, and Stephan and modified by Duwez (Reference 4) is shown in Figure 32. Here the minimum calcia content for complete stabilization of the cubic phase is indicated to be about 15 mole percent, with a two-phase monoclinic plus cubic region lying to the left of the boundary.

Using monoclinic determinations obtained by x-ray diffraction of various calcia stabilized grades, approximations of the location of this cubic boundary have been made (lever rule), and these are shown on a suggested revised phase diagram in Figure 33. Placement of the boundary cannot be made with real confidence because of the limited number of analyses available; however, there is strong evidence from lack of inversion behavior in thermal expansion curves for all but the lowest calcia grades that the cubic boundary should be displaced significantly toward the zirconia side (left side) of the diagram.

It is presumed that these differences in stabilizer effectiveness may be attributable to unintentional impurities. Material used by Vought contained in the vicinity of 1 percent impurities. Duwez reported the impurity level of his material to be less than 1 percent, but not specified further.

The difference is not believed to be due to thermal history. Duwez (reference 4) exposed a number of specimens to very long-time reheats, and found no significant change in structure occurred as a result of the isothermal treatments (ranging from 336 hours at 2510°F to 2011 hours at 1480°F).

Inasmuch as highly thermal shock resistant bodies are of considerable importance and these formulations fall in the low-calcia region of the phase diagram, it is important that more complete information on factors affecting stabilization be developed.

Thermal Expansion - Thermal expansion tests give a sensitive indication of the degree of stabilization achieved and the permanent effect of environments, as well as effects due to forming methods, grain size, and curing temperatures.

Examination of the thermal expansion curves of the work reported here reveals:

FIGURE 32 - ZrO_2 - CaO (DUWEZ ET AL)

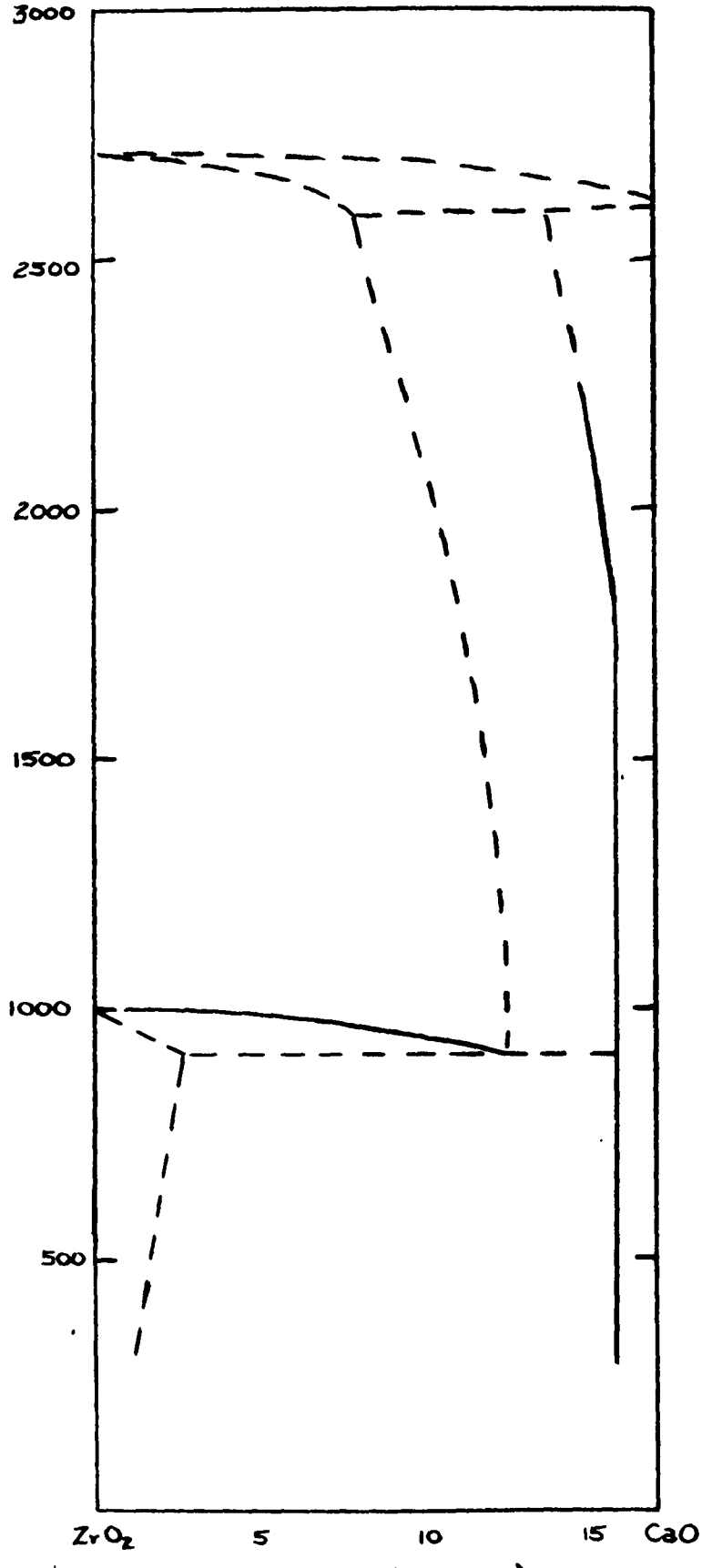
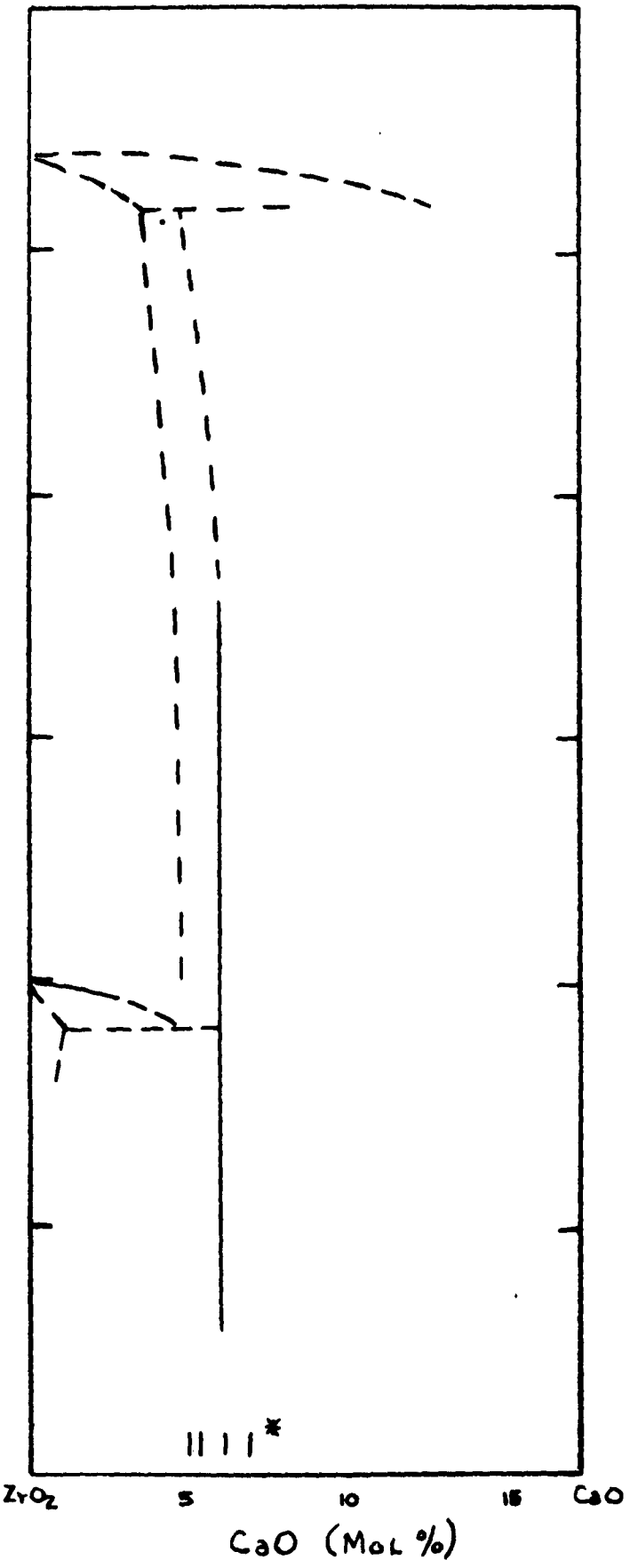


FIGURE 33 - ZrO_2 - CaO (SUGGESTED)



1. An irregularity in the neighborhood of 3500 - 4000°F exists on several expansion curves. This is thought to be due to formation of the triagonal crystal from prolonged heating at high temperatures. According to Campbell (Reference 6) this occurs above about 3600°F.

2. The shrinkage experienced on all specimens is probably due to additional sintering.

3. By comparing Figure 2 to Figure 7, it appears from the curve that increasing the particle size decreases the coefficient of thermal expansion when heating and cooling around 1500°F, and that finer particles cause a decrease in the coefficient when heating above the slight inversion temperatures and when cooling at 3500°F. These irregularities are probably the result of slight differences in chemical composition, differences in particle size, and variation in test exposure times (Table 27).

It may be pointed out that the shrinkage for the coarse grain material is greater than that of the fine grain material. This is most likely due to prior treatment (shrinkage removal obtained by the sintering before re-grinding) of all materials and the larger open porosity of the coarse material.

4. The coefficient of thermal expansion for the heterogenous zirconia (Figure 14) below the inversion temperature range is between the coefficient of stabilized zirconia and that for pure zirconia. Turner (Reference 7) has shown that this average thermal expansion coefficient of a heterogenous body may be calculated if there is no separation between the phases due to the thermal stresses.

5. As noted from Figures 1, 2, 7, 10, 14, 21, 22, and 27 at values of about 1500°F, the overall effect of increasing the degree of stabilization is to increase the thermal expansion coefficient.

Thermal Conductivity - Thermal conductivity measurements were made to show variations due to density, grain size, and method of forming. Examination of the thermal conductivity curves reveals the following general observations and notes:

1. The effect of the forming method on thermal conductivity may be seen by comparing Figures 8 and 11. The materials represented by these two figures are the same except for this parameter. The extruded specimen exhibits a lower conductivity than the molded specimen. It might be expected to be anisotropic to a small degree. The heat flow during test was perpendicular to the direction of extrusion.

2. The effect of grain and pore size is significant above 3000°F. Pores decrease conductivity at low temperatures when solid conductivity is dominant and increase conductivity at high temperatures where radiation across the pores is dominant.

3. Effective radiation conductivity across pores increases as the cube of the absolute temperature, according to Kingery (Reference 8) and increases strongly with increasing pore size. Comparing the lime stabilized materials represented by Figures 3, 8, 9, and 11, it is seen that this effect varies from negligible for the fine grain texture to very strong for the 25% porosity composition. The decrease above 3500°F for the 25% porosity composition is not fully understood, but is probably linked with the sharp decrease in emittance at this point, as exhibited for a similar material in Figure 5. This effect would not be expected to be as apparent with the lesser porosities, since their radiation component would become dominant at higher temperatures where emittance changes less rapidly.

4. Another radiation effect on conductivity exists (Reference 8). It is radiant heat transfer through the solid material, as apparently conductivity increases as the transparency increases. Transparency is a function of the optical absorption and scattering properties of the material, which in turn depend on grain size, index of refraction, and chemical composition. Not enough is known about these properties to be able to predict the relative performance of the materials tested, but it is likely that this is a contributing factor to their behavior. For a given material, decreasing the grain size would increase this effect.

Emittance - The emittance results are qualified by three considerations:

1. The assumed grey body distribution in emittance can lead to substantial errors in results if the material does not conform to this ideal.

2. The method of heating could induce errors if zirconia maintains its low temperature translucency (i. e., thickness of greater than 1/8 inch is required for opacity to visible light at room temperature). Subsurface emission can be affected by the temperature gradients in the direction of heat flow, and the possibility of detecting heater emission (specimens were 1/16 - 1/8 inch thick) existed.

3. Contamination of test specimens was severe at high temperature. Below 3000°F the specimens remained basically unaltered. Between 3000°F and 4000°F subsurface melting and contamination became increasingly significant, where at 4000°F only a thin crust of surface material identifiable as zirconia remained. Above 4000°F complete contamination occurred, only residue remained which usually did not resemble the starting material.

Thermal Shock - The R factors calculated on two formulations were higher than expected when compared to the thermal shock test data. These formulations are designated as:

1. 2.90% lime and 2.66% ceria stabilized zirconia, coarse grain, molded.

2. 7.44% yttria and 0.47% lime stabilized zirconia coarse grain, extruded.

A comparison of the calculated R factors and thermal shock test data shows reasonable agreement for the other formulations.

It may be noted that the resistance equations fail to consider several obvious factors that have a major influence on thermal shock. These are density, porosity, grain size, degree of stabilization, and method of forming.

Also as stated previously, the resistance equation will not suffice for determining the shock resistance of heterogenous materials. A method may be devised for doing so by combining the weight fractions and densities of the heterogenous materials to existing equations. A similar situation exists for those materials that are only partially stabilized. A study of strength, modulus, and shrinkage over the inversion ranges would be necessary for determination of a suitable index of thermal stress resistance.

As pointed out by Kingery (Reference 2), the derivation of a single index called "thermal stress resistance" that would apply to all materials and conditions is impractical. The index must be changed depending on the material properties, service conditions, and definition of failure.

RECOMMENDATIONS

1. Re-examine the low-calcia region of the zirconia-calcia phase diagram to establish the cause for an apparent discrepancy in the minimum level required for stabilization of the cubic phase.

2. Explore fully the potential of heterogenous-mix systems as a method for effecting substantial improvements in thermal shock resistance of ceramics.

3. Initiate intensive effort, comparable to that shown by this report, for the collection and dissemination of properties of other ceramic systems having potential design usefulness.

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